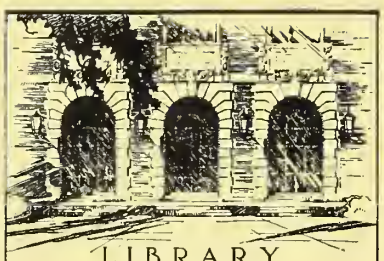

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LIQUID-VAPOR EQUILIBRIA IN THE SYSTEM AMMONIA-HYDRAZINE AT ELEVATED TEMPERATURES

R. S. Drago September 27, 1955

The liquid-vapor equilibria in the binary system ammonia-hydrazine have been measured at various compositions and at 88.5, 100.3, 114.1 and 124.9°C.

By employing teflon as a material of construction and teflon enamel as a coating material for steel, the decomposition of hydrazine which occurs on the stainless steel surfaces of the autoclave at these elevated temperatures was prevented.

Large deviations from ideality were observed in both the liquid and gas phases. Calculations showed that the deviations from ideality in the gas phase could be corrected by applying the pressure fugacity relationships for pure gaseous ammonia. The total fugacity thus obtained was broken up into the partial fugacities of ammonia and hydrazine by using a Dalton type division of the total fugacity.

Activity and activity coefficients were calculated for ammonia from the above data by choosing pure ammonia for the standard state. Activities were not calculated for hydrazine because experimental difficulties made it impossible to obtain measurements in dilute solutions. Accurate information is necessary in this region in order to determine the standard state of hydrazine in liquid ammonia solutions.

Although ammonia obeys Raoults Law over a considerable concentration range application of the activities and fugacities to the Gibbs Duhem equation indicated very large deviations from ideality by the solutions. These deviations were also reflected in the Henry's Law calculations for hydrazine. Instead of being constant the Henry's Law Ratio D (where $D = \frac{f}{[N_2H_4]}$) decreases with increase in hydrazine concentration at the four temperatures studied. This trend can be explained by assuming the association of hydrazine molecules in solution, with the amount of association increasing with increase in hydrazine concentration. It is assumed that the concentration of associated molecules becomes negligible as the amount of hydrazine present in solution becomes small and as a result the true Henry's Law constant for monomer is approached in dilute solutions. The concentration of hydrazine monomer can thus be calculated in the solutions where ammonia obeys Raoult's Law from a knowledge of the fugacity of hydrazine and the extrapolated value of the Henry's Law constant. The amount of associated material present can be obtained by difference of the total amount of material and the amount of monomer. The amount of associated

material can be converted to concentrations corresponding to the various degrees of association and the equilibrium constants between monomer and the different polymers can be evaluated. Accurate values for the equilibrium constants between monomer and the various polymers could not be obtained, however, because the lack of precise measurements in very dilute hydrazine solutions made it impossible to obtain sufficiently accurate extrapolations of the Henry's Law constant to infinite dilution.

Semiquantitative calculations support the postulate that association of hydrazine is a probable explanation for the observed trends. The approximate values calculated for the heats of association were of the order of magnitude corresponding to the weak forces of association that might be expected from hydrogen bonding between the hydrazine molecules.

Because of the complex nature of the solute in these solutions other thermodynamic data were not evaluated.

ANION EXCHANGE STUDIES. III. Ni(II) IN AQUEOUS HYDROCHLORIC ACID AND LITHIUM CHLORIDE.[1]

R. H. Herber September 20, 1953

In their extensive studies of the anion exchange behavior of the transition metals, Kraus and his co-workers[2,3] have confirmed the fact that nickel is not adsorbed from aqueous hydrochloric acid by anion exchangers of the type Dowex-1, even at concentration of 12 N acid. Herber and Irvine[4] have found similarly no adsorption of Ni(II) from solutions up to 7 N in HBr. This behavior is anomalous with respect to the neighboring transition metals all of which are at least moderately well adsorbed by anion exchangers from these solutions. It seems further to be inconsistent with the extensive complexing tendencies normally ascribed to divalent nickel.

Recent experimentation has shown that the retention of a given metal by an anion exchanger can be enhanced (a) by using LiCl rather than HCl as an elutriant[5] and (b) by using resins of high cross linkages[6]. In the light of these recent improvements in conditions for the retention of metals by Dowex-1, the anion exchange behavior of Ni(II) has been re-examined. The present research indicates clearly that even in concentrated (~8N) LiCl, and employing highly cross linked (24% Divinylbenzene) resins, no retention of Ni(II) by the exchanger was observed.

The interpretation of these results does not depend upon the formulation of a specific ion exchange mechanism, as it can be shown that the only necessary condition for ion exchange adsorption is the presence in the resin of an anionic species carrying the metal atom, and the reaction in situ of this ionic species with the fixed cationic groups of the exchanger. It appears then that the above results indicate the absence in the resin of complexes of the type $NiCl_3^-$, $NiCl_4^=$, etc.

Under the conditions employed in this study, it is known[7] that the chloride ion activity in the resins is greater than that in the ambient solution. Since the stability of the singly charged anion complex in the aqueous phase (w) and resin phase (r) can be represented by

$$(NiCl_3^-)_w \rightleftharpoons (NiCl_2)_w + (Cl^-)_w$$

$$(NiCl_3^-)_r \rightleftharpoons (NiCl_2)_r + (Cl^-)_r$$

and the activity of $(NiCl_2)_r \gtrless (NiCl_2)_w$ it can be concluded that the absence of $NiCl_3^-$ in the resin phase implies the concurrent absence of $NiCl_3^-$ in the aqueous phase.

These conclusions have been further corroborated by optical density measurements of aqueous HCl and LiCl solutions of Ni(II). It was found, in agreement with earlier investigations[8], that in concentrated HCl, an absorption peak which is absent in less concentrated acid arises at 425 mu. A plot of log (% transmission) vs. log (Cl^- activity) produced a curve which was linear above ~6M HCl with a slope of 1.00. The optical densities of the LiCl solutions were directly superimposable on the curve obtained with HCl. Even at chloride activities of 380, there was no indication of a deviation from unit slope of the above curve.

These data are considered evidences for the formation of $NiCl^+$ from the nickel ion in aqueous solution, presumably $Ni(H_2O)_6^{++}$, and for the absence - even in 12 N HCl and 8 N LiCl - of species such as $NiCl_2$ or $NiCl_3^-$. It is further concluded, that since the absorption peak of the Ni(II) solutions at 350 mu, which is presumably due to the $Ni(H_2O)_6^{++}$ ion, falls only ~15% in solutions 11 N in HCl as compared to the value in pure water, that only a small percentage of the metal is present in the form of $NiCl^+$, most of it remaining as the hexahydrated species. This conclusion is consonant with the non departure from linearity of the log (% transmission) vs. log (Cl^- activity) at 425 mu even in 11 N HCl or 8 N lithium chloride, as well as with absorption data taken on perchloric acid solutions of $NiCl_2$.

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PROBLEMS IN CALORIMETRY

L. L. Miller, Jr. October 4, 1957

A calorimeter has been constructed to measure specific heats, heats of solution, heats of reaction and other thermal energy in liquid systems. In this calorimeter isothermal control is used for endothermic processes, while adiabatic control is used for exothermic processes. In the measurement of specific heats, control similar to adiabatic control is used.

Historically, adiabatic calorimetry was initiated in 1905 by T.W. Richards and co-workers. The design of adiabatic calorimeters has remained basically unchanged since then, improvements in design being largely directed towards reducing thermal lags within the calorimeters and towards increasing sensitivity of response. On the whole, relatively little work has been done in this field, presumably because of experimental difficulties.

In the calorimeter we have recently assembled, the recording and control of temperatures is continuous and largely automatic. The recording of heat input to the calorimeter is also automatic and is done by means of an integrating watt-second meter. The principles of operation of the instrumentation required to carry out these recording and control processes is described.

At the present time, all components of the calorimeter operate satisfactorily. In order to effect improvements in accuracy, we have spent considerable time recently experimenting with the design of the resistance thermometers used to detect temperatures. These thermometers have been picking up stray currents due to insufficient electrical insulation on the heater elements. Various chemically resistant coatings, made from materials such as Teflon, silicone resins, polyethylene films and other resins are being examined at present to find a coating which will be as chemically inert as possible and yet have a resistance of the order of 50-100 megohms

When this is done, we plan to examine specific heat curves for a series selected liquids and to start studies of the heats of reaction of several different chemical processes. Because of the nature of the recording and control apparatus, the present instrument is particular suited to the study of slow reactions with complex reaction mechanisms.

Ag(II)O AS AN OXIDANT

Kaye L. Motz October 11, 1955

The nitrate complex $Ag_7O_8NO_3$ was discovered by Ritter in 1804. Later Watson decomposed this complex to obtain AgO. Using persulfate instead of anodic oxidation Austin[2] obtained the first relatively pure AgO.

Yost[3] discovered a compound Ag_2O_3 while working on catalytic effects of Ag. Carman argued for a Ag(III) species as the primary one in silver catalysis and proposed the following mechanism:

$$Ag(III) + Ag(I) \rightarrow Ag(II)$$

A classic study by Noyes[5,6,7,8,9] demonstrated conclusively that Ag(II) is the primary species existing in solution. After studies using O_3 on silver salts he postulated:

$$Ag^+ + O_2 \rightarrow AgO^+ + O_2 \quad \text{(slow rate)}$$

$$2H^+ + AgO^+ + Ag^+ \quad 2Ag^{++} + H_2O \quad \text{(rapid equilibrium)}$$

Ag^{++} forms a soluble nitrate complex[10] and stable, solid complexes[11] with pyridine, a,a'dipyridyl, orthophenanthroline, tripyridyl, picolinic acid, and quinolic acid.

AgF_2 and AgO are the only simple Ag(II) compounds known to exist. Silver(II) fluoride is a strong oxidizing agent and a good fluorinating agent. Silver(II) oxide has been prepared (a) chemically by the use of persulfate, lead dioxide, bismuth dioxide, ozone, hypochlorite and (b) electrochemically by anodic oxidation.

The oxidizing strength of Ag(II) is shown by the following oxidation potentials[12].

$$Ag^+ \rightarrow Ag^{++} + e \quad E = -1.927 \text{ (4M } HNO_3\text{)}, \ -1.970 \text{ (4M } HClO_4\text{)}$$

$$Ag^+ \rightarrow Ag^{++} + e \quad E^\circ = 1.98 \text{ (by extrapolation)}$$

$$2OH^- + Ag_2O \rightarrow 2AgO + H_2O + 2e \quad E_B^\circ = -0.57$$

The presence of silver catalyzes the oxidation of Cr^{+++}[3], NH_3[3], halides[3] and VO^{++}[13]. The conversion of ethylene to ethylene oxide entails use of AgO as a catalyst[14].

Study of the behavior of AgO in alkaline solution began in 1950[15]. Recently Dutta[16,17,18] has prepared AgO by NaOCl treatment of silver salt in alkaline solution.

Oxidation of $Na_2S_2O_3$ by AgO can lead to the dithionate trithionate, tetrathionate or mixtures of all three. Before estimation of AgO could be effected the product had to be determined.. Using mole ratios of reactants and products the following appears to be the primary reaction:

$$3Na_2S_2O_3 + 8AgO + H_2O \rightarrow 2Na_2S_3O_6 + 2NaOH + 4Ag_2O$$

followed by the secondary reaction:

$$Na_2S_3O_6 + 4NaOH + 8AgO \rightarrow Na_2SO_4 + 4Ag_2O + 2H_2O$$

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CONDENSED PHOSPHATES AS ION EXCHANGE RESINS

Chui Fan Liu October 18, 1955

The condensed phosphates have been the subject of many investigations because of their numerour technical applications. A very well known property of the polyphosphates is their ability to tie up alkali earth ions such as Ca^{++} and Mg^{++} and to keep them in solution. This is usually explained by complex formation between the cation and the polyphosphate anion (1). However, Thilo and Rattay (2), on the basis of titration studies, concluded that the sequestering action of the polyphosphate is due to an ion exchange phenomenon.

Van Wazer et al (3),(4),(5) have shown by pH titrations and viscosity measurements that the polyphosphate anions exist in solution as linear polymers without any chain branching. This hypothesis has gained support from light scattering experiments carried out by Strauss et al(6). Thilo's(7) hydrolysis experiments also confirm this postulate.

The long chain polyphosphates (alkali salts or the corresponding acids), due to their high charges, are only partially dissociated in aqueous solution (about 25% dissociated). This fact was shown by Wall and Doremus(8) by conductivity and transference number measurements.

Thilo and Rattay(2) studied a series of polyphosphates of the Grahm's salt type as to their abilities to sequester calcium and magnesium ions. The data were obtained by titrating polyphosphate solutions with the alkali earth chloride solutions until permanent precipitation occurred. They found that with increased concentration of polyphosphate the amount of polyphosphate necessary to keep a definite quantity of Ca^{++} in solution increased. Quantitatively, the amount of Ca++ kept in solution followed the Freundlich adsorption isotherm. This was taken as evidence for a continuous ion exchange phenomenon rather than the formation of complexes whose solubility curves should show definite breaks. The alkali salts, the ammonium salt, and the free polyphosphoric acid behaved in a similar manner. On the basis of their results the authors set up the following series for increased cation binding power:

$$K < NH_4 < Na < H < Li$$

At concentrations of polyphosphate lower than 4m mol/l, however, the series became

$$K < Li < Na < H < NH_4$$

The sequestering power of the polyphosphate solutions were also altered by the addition of another electrolyte. At concentrations higher than 4m mol/l the addition of NaCl decreased the cation binding power of the polyphosphate. This, of course, is in accordance with the ion exchange concept. However, the authors were not able to explain why the effect of the addition of NaCl was reversed when the concentration of the polyphosphate was lower than 4m mol/l.

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THIONYL CHLORIDE AS AN IONIZING SOLVENT

S.M. Chodosh October 25, 1955

Physical Constants of Anhydrous $SOCl_2$:

Boiling Point (760 mm)	75.6°C.
Melting Point (1 atm)	-104.5°C.
Molvolume at 20°C	72.5c.c.
Dielectric Constant at 20°C	9.05
Dipolemoment	1.58 Debye
Specific Electrical Conductivity at 20°C	$3.5 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$

Thionyl chloride undergoes self-ionization as follows:

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^- \rightleftharpoons SO^{++} + 2Cl^-.$$

The specific conductivity at 20°C is $3.5 \times 10^{-9}\ \Omega^{-1} cm^{-1}$ and is assumed to be due to the formation of the $SOCl^+$ and Cl^- ions; further dissociation is so slight that it need not be considered.

Heteropolar substances are slightly or not at all soluble in $SOCl_2$, whereas homopolar substances are quite soluble in $SOCl_2$ solution. Increase in conductivity occurs when certain compounds are dissolved in $SOCl_2$, thus indicating that such solutes are electrolytically dissociated. Many of these compounds may be regarded as solvo-bases, ansolvo-bases, ansolvo-acids, ampholytes, or solvosalts. Solvo-bases are believed to increase the chloride ion concentration of the solvent; ansolvo-bases combine with the SOCl+ ion and increase the concentration of chloride ion; ansolvo-acids form chloride complexes and in so doing increase the concentration of SOCl+ ion. Ampholytes can increase either the Cl^- or SOCl+ concentration, whereas solvo-salts dissociate to yield ions differing from those furnished by the solvent.

Solvo-Base	Ions in $SOCl_2$ Solution
$[(C_2H_5)_4N]Cl$	$(C_2H_5)_4N^+$, Cl^-
$HgCl_2$	$HgCl^+$, Hg^{++}, Cl^-
Ansolvo-Base	
$(C_2H_5)_3N$	$[(C_2H_5)_3NSOCl]^+$, Cl^-
C_5H_5N	$[(C_2H_5NSOCl]^+$, Cl^-
Ansolvo-Acid	
$SbCl_5$	SOCl+, $[SbCl_6]^-$
$FeCl_3$	SOCl+, $[FeCl_6]^-$
Amphoteric Electrolytes	
$TiCl_4$	$(TiCl_2)^{++}$, Cl^-
	SOCl+, $[TiCl_6]$
PCl_5	PCl_4^+, Cl^-
	SOCl+, $[PCl_6]^-$
Solvo-Salt	
$[(C_2H_5)_4N]I$	$[C_2H_5)_4N]^+$, I^-
I_2	I^+, I^-

A plot of molecular conductivity versus dilution demonstrates that the substituted ammonium compounds are the strongest electrolytes of all compounds investigated in $SOCl_2$ solution. Pyridine and organic nitrogen bases are unique since at increasing concentrations the molecular conductivity rises. This is ascribed to association followed by dissociation.

Conductiometric titrations have been performed which illustrate solvo-neutralization in $SOCl_2$ solution. The cation of the ansolvo-acid reacts with the anion of the solvo or ansolvo-base to form a soluble or an insoluble salt.

1. The titration of the weak solvo-base $HgCl_2$ in $SOCl_2$, with $SbCl_5$ in $SOCl_2$ yields two end points:

Mole Ratio Titrant to Solute	Reaction
1:1	$HgCl_2 + SOCl[SbCl_6] = HgCl[SbCl_6] + SOCl_2$
2:1	$HgCl[SbCl_6] + SOCl[SbCl_6] = Hg[SbCl_6 + SOCl_2$

2. Titration of the moderately strong solvo-base, $(C_2H_5)_4NCl$, with $SnCl_4$:

0.5	$2(C_2H_5)_4NCl + (SOCl)_2[SnCl_6] = [(C_2H_5)_4N]_2\cdot[SnCl_6]\downarrow + 2SOCl_2$
1	$[(C_2H_5)_4N]_2\cdot[SnCl_6] + (SOCl)_2[SnCl_6] = 2[(C_2H_5)_4N](SOCl)\cdot[SnCl_6]$

3. Titration of the weak ansolvo-acid, $AlCl_3$, with $(C_2H_5)_4NCl$

1	$(C_2H_5)_4NCl + (SOCl)[AlCl_4] = [(C_2H_5)_4N][AlCl_4] + SOCl_2$

4. Titration of the ampholyte, $TiCl_4$, with $[(C_2H_4)_4N]Cl$.

1	$(SOCl)_2[TiCl_6] + (C_2H_5)_4NCl = SOCl_2 + [(C_2H_5)_4N](SOCl)\cdot[TiCl_6]$
2	$(SOCl_2)[TiCl_6] + 2(C_2H_5)_4NCl = 2SOCl_2 + [(C_2H_5)_4N]_2\cdot[TiCl_6]$

5. Titration of the ampholyte, $TiCl_4$, with $SbCl_5$

1:2	$(TiCl_2)Cl_2 + 2(SOCl)\cdot[SbCl_6] = 2SOCl_2 + (TiCl_2)[SbCl_6]_2$

Ebullioscopic molecular weight determinations show that the von't Hoff factor i, the ratio of experimental to the theoretical molecular weight is dependent on dilution. Values of i greater than one indicate dissociation; values less than one, association. However, when i is less than one and the conductivity of the pure solvent is raised by the solute then both association and dissociatio occur with the former being more important. Triethylamine, pyridine, and quinoline reveal with increasing concentration, a reduction of the i-factor and an increase in molar conductivity. It is concluded

that the associated molecules are more strongly dissociated than the simple molecules. The tendency for association increases in the order triethylamine, pyridine, and quinoline.

Potentiometric titrations employing a molybdenum indicator electrode were performed in order to verify conductiometric titrations which showed that $SbCl_5$ and $AlCl_3$ are "univalent", $SnCl_4$ is a "divalent", and $SbCl_3$ and $FeCl_3$ are "trivalent" ansolvo-acids in $SOCl_2$ solution. It was also demonstrated potentiometrically that PCl_5 is a "univalent" ampholyte and that $TiCl_4$ behaves as a "divalent" ampholyte.

The solvolysis of iodide proceeds according to the following equations:

$$a.\quad 2I^- + SOCl_2 \rightleftarrows SOI_2 + 2Cl^-$$
$$b.\quad 2SOI_2 \rightleftharpoons SO_2 + S + 2I_2$$

A method of preparation of $(C_2H_5)_4NCl$ from a solution of $(C_2H_5)_4NI$ is proposed.

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TRISULFIMIDE

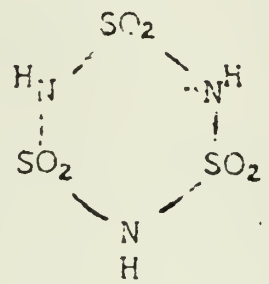
W.E. Bull

November 1, 1955

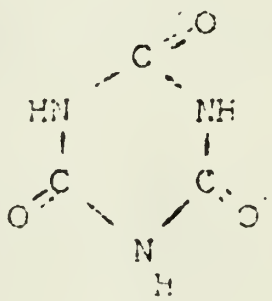
Traube (1) in 1892 isolated from the reaction products of sulfuryl chloride and ammonia, a number of salts which he believed to be derivatives of the imide of sulfuric acid, $HN{=}SO_2$. In a later publication (2) Traube reported that an aqueous solution of the residue obtained after holding the temperature of sulfamide above its melting point for several hours contained "sulfimide". He formulated the reaction as a deammoniation process.

$$SO_2(NH_2)_2 \rightleftharpoons NH_3 + SO_2NH$$

Hantzsch and Holl (3) concluded subsequently from molecular weight determinations of the methyl derivative of "sulfimide" that the free imide exists as a trimer in solution. These workers also thought they had obtained the free imide as a white crystalline substance. Hantzsch and Stuer (4) later proved this substance to be imidodisulfamide $NH(SO_2NH_2)_2$. Hantzsch and Holl were the first to note the resemblance of trisulfimide to cyanuric acid and to suggest an analogous structure.



Trisulfimide



Cyanuric Acid

Trisulfimide has also been suggested to be a decomposition product of sulfamyl chloride (5). The silver salt $(AgNSO_2)_3$ has been obtained in 20% yields from the reaction products of SO_2Cl_2 and $NaNH_2$ (6). More recently tetrasulfimide derivatives, as well as trisulfimide derivatives, were obtained from the reaction products of SO_3 and NH_3 in an inert solvent (7).

Heinze and Meuwsen (8) have just recently further investigated trisulfimide. During their studies they have found that if the temperature of sulfamide is kept between 180° and 200°C, it rearranges to ammonium trisulfimide without loss of ammonia.

$$3SO_2(NH)_2 \rightarrow (NH_4NSO_2)_3$$

These workers prepared various heavy metal salts including hexammine cobalt III trisulfimide which they suggest as a possible qualitative test. A benzidine derivative of the trisulfimide was prepared and the analysis found to correspond to the composition $[NH_2C_{12}H_8NH_2]_5[SO_2NH]_3 \cdot 5H_2O$.

The following structure is postulated:

Trisulfimide hydrolyzes readily in aqueous solution to form as the primary reaction products sulfuric acid and imidodisulfamide yields sulfamic acid and sulfamide. The hydrolysis seems to be catalized by the presence of acid.

Conductometric and potentiometric titration curves of aqueous solutions of trisulfimide versus NaOH resemble those obtained from a mixture of a strong and a weak acid. The first significant break occurs when a ratio of two moles of base have been added per mole of trisulfimide. This finding would indicate that trisulfimide contains 2 strongly acidic hydrogen atoms and one very much weaker hydrogen atom.

Heinze and Meuwsen have isolated a material which they believe to be a mixture of the free trisulfimide and the triethyltrisulfimide. The anhydrous silver salt was added in slight excess to an anhydrous etheral HCl solution. The precipitated AgCl was removed; upon evaporation of the residual solution a hygroscopic resin was obtained. A freshly prepared aqueous solution of this resin was sulfate free. Upon analysis, the S to N atomic ratio was found to be 1:1.03 and to contain organic constituents up to about 12%. The resin was quite soluble in H_2O, MeOH and EtOH.

X-ray crystal structure studies of $(AgNSO_2)_3 \cdot 3H_2O$ carried out very recently have confirmed the previously postulated structure of trisulfimide as a six membered ring composed of alternating N and S atoms (9).

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DERIVATIVES OF $(SO_2NH)_3$

	Form	Solubility	Stability	Ref.
$(AgNSO_2)_3 \cdot 3H_2O$	hexagonal crystals	0.1 g/100 ml. H_2O 0°	$-H_2O$, 110°	(1,7,8)
		0.7 g/100 ml. H_2O 100°		
		Insol. EtOH and Et_2O		
$(NH_4NSO_2)_3$	white crystalline	v.sol. H_2O, Insol. EtOH	d. >210°	(2,7)
$(NaNSO_2)_3$	white powder	v.sol. H_2O	d. on heat	(2)
$(KNSO_2)_3$	colorless needles	v.sol. H_2O	d. on heat	(2)
$Ca_3[(NSO_2)_3]_2$		v.sol. H_2O		(2)
$Ba_3[(NSO_2)_3]_2$	fine needles	v.sol. H_2O	d. on heat	(2)
$Cu_3[(NSO_2)_3]_2$	green powder			(2)
$[TlNSO_2]_3$	flake-like crystal	sol. hot H_2O, Insol. EtOH, Et_2O		(7)
$[Hg(I)NSO_2]_3$	micro needles	sol. dil. HNO_3		(7)
$(Hg(II))_3[(NSO_2)_3]_2$	colorless crystals	sol. dil. HCl		(7)
		Insol. 2N HNO_3, H_2O, EtOH, Et_2O $Me_2C{=}O$		
$Pb_3[(NSO_2)_3]_2$	colorless fine needles	sol. dil. HNO_3		(7)
$Co(NH_3)_6(NSO_2)_3$	yellow-orange	v.insol. H_2O sol. 1% HCl		(7)
$(Cl_3NSO_2)_3$	colorless prisms	insol. H_2O sol. Et_2O, EtOH Benzene	M.p. 120°	(3,7)
$(C_2H_5NSO_2)_3$	colorless prisms	insol. H_2O sol. Benzene, EtOH and Et_2O	M.p. 65-66°	(7)
$(C_6H_5CONSO_2)_3$	colorless crystals		M.p. 112°	(3)
$[H_2NC_{12}H_8NH_2]_5$				
$[HNSO_2]_3 \cdot 5H_2O$	colorless needles	insol. cold H_2O insol. dil. acids		(7)

METAL THIONITROSYLATES

G.L. Johnson November 8, 1955

For some time, it has been known that NO can serve as a ligand for many heavy metal atoms. If the oxygen of NO is replaced by sulfur, one obtains a compound with the composition NS of which the tetramer, $(SN)_4$, is best known. It is conceivable that S_4N_4 would split into two radicals of the formula [•N=S-S-N=S•] or into four radicals of the formula [•N=S] or into the ions, $[N{=}S]^-$ and $[N{=}S]^+$. If such radicals or ions do exist, one should be able to prepare complex salts in which the NS group is present as a ligand.

Goehring and Debo[1] succeeded in obtaining $[Ni(NS)_4]$ from $[Ni(CO)_4]$. They suspect that this compound exists both as a polymer and a monomer. Daum, Goehring, and Weiss[2] have prepared the analogous cobalt compound, $[Co(NS)_4]$, and have shown that the absorption spectra of the cobalt and nickel compounds are similar. Goehring and co-workers[2] believe that the N-S ring is split in the formation of these complex compounds. However, they do not discredit the possibility that the ring is not broken.

Goehring and Berg[3] studied the reaction of S_4N_4 with potassium in liquid ammonia. They believe S_4N_4 reacts with ammonia to form an ammoniate.

$$N^-{=}S^+{-}N{=}S \longleftrightarrow N^-{=}S^+{-}N^-{-}S^+ + KNH_2 \rightarrow H{-}N{=}S^+{-}N^-{-}S{-}NH_2$$

$$H{-}N{=}S^+{-}N^-{-}S{-}NH_2 \rightarrow H{-}N{=}S + H{-}N{=}S^+{-}N^-{-}H$$

In liquid ammonia, these acid imides will react with bases such as KNH_2 to form salts.

$$HNS + (NH)_2S + 3KNH_2 \rightarrow KNS + (KN)_2S + 3NH_3$$

Goehring and Berg prepared the salt of the composition $K_3N_3S_2$. They believe this salt to be an equi-molar mixture of KNS and $(KN)_2S$. In 1904, Ruff and Geisel[5] suspected that an ammoniate of S_4N_4 was the intermediate in the preparation of insoluble lead and mercury salts of the composition $HgN_2S{\cdot}NH_3$ and $Pb(NS)_2{\cdot}NH_3$.

Goehring, Weiss, and Zirker[4] prepared $Pb(NS)_2$ and $Tl(NS)_3$ from a liquid ammonia solution of S_4N_4. $Tl_3(NS)_6$, $Cu(NS)_2$, and $Ag(NS)_2$ were prepared by reacting the appropriate metal salt with the ammoniate of S_4N_4 in an organic solvent such as pyridine or alcohol. Goehring and co-workers[4] also prepared Cu(NS) and Ag(NS) by reacting the metal salt with $S_4(NH)_4$ in pyridine. They were unable to prepare the Cu(I) and Ag(I) thionitrosylates from the ammoniate of S_4N_4 because of its oxidizing ability. Meuwsen and Lösel[5] prepared $Hg_5(NS)_8$ and $Hg(NS)_2$ from the reaction of Hg(II)acetate with $S_4(NH)_4$ in pyridine.

They speculate that the $Hg_5(NS)_8$ is a mixture of $Hg(NS)_2$ and $Hg_2(NS)_2$ in a ratio of three to one. These compounds are, in general, highly colored and soluble in organic solvents. They will decompose when treated with acids or bases and when subjected to heat or shock.

The color of these compounds indicate that they are essentially covalent materials. Goehring, Weiss, and Zirker[4] believe the metal is bound through the nitrogen. They base this, in part, on the following observations:

$$Ag(NS) + C_2H_5I \rightarrow AgI + C_2H_5NS$$
$$C_2H_5NS + 4H \rightarrow C_2H_5NH_2 + H_2S$$

It is not certain in all of the above compounds if the NS ring is split. However, Goehring and co-workers[4] feel there is evidence to prove that ring rupture has occurred in formation of $Pb(NS)_2$, $Cu(NS)_2$, $Tl(NS)_3$, and $Ag(NS)_2$.

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STUDIES ON THE ELECTROCHEMISTRY OF SILICATE MELTS

P.N. Yocom November 15, 1955

The purpose of this work has been to determine th type of conductance found in silicate melts of different basicities and to obtain values for the transport numbers. From transport numbers and known conductance data, it is possible to get a picture of what happens when an electric current passes through a silicate melt and to obtain a quantitative connection between conductance and composition.

Previous investigations by Bockris et al[3,5] have shown that the alkali and alkaline earth silicates are wholly ionic conductors. Since little information had been made available concerning silicate melts of other metals, the following systems were investigated by the moving boundary method for the determination of the degree of applicability of Faraday's Law.

Bottom electrolyte dark	Top electrolyte white
2.00 $FeO \cdot SiO_2$	$Li_2O \cdot CaO \cdot SiO_2$
1.33 $FeO \cdot 0.67\ CaO \cdot SiO_2$	$Li_2O \cdot CaO \cdot SiO_2$
2.50 $CoO \cdot SiO_2$	1.25 $CaO \cdot 1.25$ [illegible] $\cdot SiO_2$
2.75 $CoO \cdot SiO_2$	1.25 $CaO \cdot 1.50\ BaO \cdot Si$[illegible]
3.00 $CoO \cdot SiO_2$	1.50 $CaO \cdot 1.50$ [illegible] $\cdot Si$[illegible]

The degree of ionic conduction was calculated from the following formula:

$$I\ (f/F) = \pi r^2 hd/E$$

where d = density of lower electrolyte
E = equivalent weight molecular weight/4
r = radius of the tube
h = distance the boundary has travelled
f = quantity of electricity passed
F = 96,500 coulombs
I = degree of ionic conductance

The following table gives the results of the conductance measurements. It will be noted that the type of conduction changes from ionic to semi-conduction as the basicity increases.

Composition	Temp. °C	Coulombs passed	Change of Boundary mm	Ionic conductance
$2FeO \cdot SiO_2$	1210	840	7.8	0.95
$2FeO \cdot SiO_2$	1300	715	10.8	0.99
$2FeO \cdot SiO_2$	1400	1120	5.9	0.[illegible]
1.33 $FeO \cdot 0.67\ CaO \cdot SiO_2$	1250	660	4.6	1.04
2.50 $CoO \cdot SiO_2$	1440	106	4.7	0.95
2.75 $CoO \cdot SiO_2$	1450	171	6.0	0.72
3.00 $CoO \cdot SiO_2$	1450	239	0.0	0.00

The products of electrolysis are the metal at the cathode and SiO_2 and O_2 at the anode. The SiO_2 formed at the anode causes the resistance across the melt to increase continuously.

Certain difficulties are encountered in the determination of transport numbers in melts which, unlike solids and liquid solutions, have no frame of reference with which changes in concentration or boundary can be compared. However, it was found possible to determine transference numbers in melts if an excess of the basic oxide is taken as a reference. If this excess is not too large, as in the mixture 2.5 $CoO \cdot SiO_2$, ionic conductance was found to prevail but only 2 Co^{+2} had migrated. The analysis of the volume swept out by the boundary showed that 0.5 Co remained in it and had been mixed with the part of the top electrolyte that had migrated. This shows that the excess cobalt in the bottom electrolyte must be dissolved in the orthosilicate as an unionized oxide. By the use of this method of excess oxide, the cation transport number was found to be one. This agrees with the findings of Bockris et al[3,5] for the alkali and alkaline earth silicates.

According to the hole theory, the structure of a liquid is believed to resemble that of the corresponding solid.[6] This theory makes it possible to interrelate conductivity and composition of silicate melts. Ionic conduction has been shown to be due to the cations only; this observation is the basis for the assumption that conduction is due to extensive Frankel disorder (large immobile anions and small mobile cations).

The silicates are divided into three groups which depend upon the number of interstitial sites allowed to the migrating cations by the silicon oxygen structure. The disilicates with the composition $(Si_2O_5)^{=}$ are two dimensional sheets with interstitial sites only between sheets. Defect factor = 1. The metasilicates with composition $(SiO_3)^{=}$ are one dimensional chain with twice as many interstitial sites as the disilicates. Defect factor = 2. The orthosilicates with the composition $(SiO_4)^{4-}$ are spatially restricted groups with three times the number of interstitial sites as the disilicates. Defect factor = 3.

Since cationic conductance occurs exclusively, specific conductance may be represented by an expression which is analogous to the customary expression for solids,

$$x = n z^2 e^2 u S$$

x = specific conductance
n = number of cations/ml
ze= charge of the ions
u = mobility of the migrating particles in disilicates under unit force
S = defect factor.

If, for instance, the conductance of a disilicate is known, it becomes possible to calculate the conductance of any other composition provided the defect factor is also known. Thus

$$x_1 = (n_1/n_2)\ x_2\ (S_1/S_2)$$

The following results were calculated from the above formula; the observed values were obtained by Bockris et al[5].

Composition	Defect Factor	Conductivity ohm^{-1} cm^{-1} computed	observed
$MgO \cdot 2SiO_2$	1	-	0.23
$MgO \cdot SiO_2$	2	0.77	0.72
$2MgO \cdot SiO_2$	3	1.74	2.15
$CaO \cdot 2SiO_2$	1	-	0.31
$CaO \cdot SiO_2$	2	0.98	0.99
$2CaO \cdot SiO_2$	3	2.05	1.15
$SrO \cdot 2SiO_2$	1	-	0.21
$SrO \cdot SiO_2$	2	0.63	0.63
$2SrO \cdot SiO_2$	3	1.3	1.4
$BaO \cdot 2SiO_2$	1	-	0.18
$BaO \cdot SiO_2$	2	0.53	0.60
$2BaO \cdot SiO_2$	3	1.0	1.32

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ORGANOMETALLIC DERIVATIVES OF THE TRANSITION METALS

G.W. Griffin November 22, 1955

Organic, as well as inorganic chemists have long been interested in preparing stable organometallic derivatives of the transition elements.[1,2,3,4,5] Many attempts to prepare such derivatives appear in the literature, but with the exception of tetramethylplatinum[3], no stable transition metal organics are known in which all of the valences of the metal are satisfied by organic groups.

It is interesting that carbon monoxide, cyanides and isonitriles form stable carbon bonds with the transition metals, while alkyl and aryl groups do not. Pauling[6] has suggested that the stability of compounds such as $Ni(CO)_4$ might be attributed to participation of the d electrons of the metal to form multiple covalent linkages with the electron accepting ligand as indicated in (c).

a) $-Ni^{\ominus}-C\equiv O^{\oplus}$

b) $-Ni^{\ominus}-\overset{\oplus}{C}=O$

c) $-Ni=C=O$

This postulate gains support from the observation that the bond distances in these and other similar complexes are shorter than those expected for single covalent bonds as represented in (a) and (b). Structure (c) is also more satisfying than (a) or (b), since the negative charge is removed from the metal, a state which should be more favorable for such electropositive elements. It is not assumed that (c) represents the true structure of $Ni(CO)_4$, but rather that it is one of three contributing structures.

Nast[7,8] used Pauling's suggestion as a working hypothesis to predict the formation of alkynyl derivatives of the transition metals; he succeeded in preparing such substances. The stability of these compounds, like that of the metal carbonyls, is attributed to the contribution of structure c' to the hybrid:

$\overset{\ominus}{Ni}-C\equiv C-R$ $\qquad$ $\overset{\ominus}{Ni}-\overset{\oplus}{C}=\underline{\overset{\ominus}{C}}-R$ $\qquad$ $Ni=C=\underline{\overset{\ominus}{C}}-R$

a' $\qquad$ b' $\qquad$ c'

The preparation of alkynyl complexes from thiocyanates in liquid ammonia is represented in the following typical reaction scheme,

in which nickel is the transition metal:

$$4MC{\equiv}C\text{-}R + [Ni(NH_3)_6](SCN)_2 \rightarrow M_2[Ni(\text{-}C{\equiv}C\text{-}R)_4] + 2MSCN + 6NH_3$$

Complexes which have been prepared in this manner include the following highly colored compounds:

$K_2[Ni(\text{-}C{\equiv}CH)_4]$	$K_2[Ni(C{\equiv}C\text{-}CH_3)_4]$	$K_2[Ni(\text{-}C{\equiv}CC_6H_5)_4]$
$[Ni(\text{-}C{\equiv}CC_6H_5)_2]_x$	$[Ni(\text{-}C{\equiv}CH)_2 \cdot 4NH_3]$	$Na_2[Ni(\text{-}C{\equiv}CH)_4] \cdot 2NH_3$
$K_4[Ni(\text{-}C{\equiv}CH)_4]$	$K_2[Ni(\text{-}C{\equiv}CH)_3]$	$Na_2[Ni(\text{-}C{\equiv}CC_6H_5)_4]$
$Na_3[Co(C{\equiv}C\text{-}CH_3)_6]$[9]	$K_3[Cr(C{\equiv}CH)_6]$[10]	$Na_4[Co(C{\equiv}C\text{-}CH_3)_6]$

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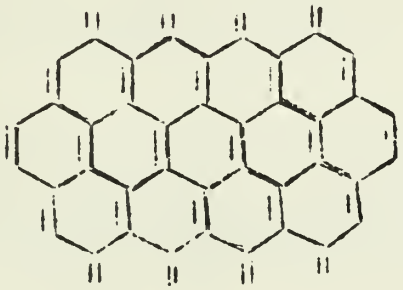
INCLUSION COMPOUNDS OF GRAPHITE

D.S. Smith November 29, 1955

Graphite has the structure of a two-dimensional giant molecule consisting of sheets of regular hexagons, (1),(2),(3). The linkage between atoms in the basal plane possesses about 1/3 double bond character, making the structure quinone-like (two double bonds per hexagon).



(one of several resonance forms)

The interatomic distance in the basal plane is 1.42 Å whereas planes are separated by 3.41 Å. This accounts for the directional characteristics of graphite and thus for the tremendous differences between the diamond and graphite forms of carbon.

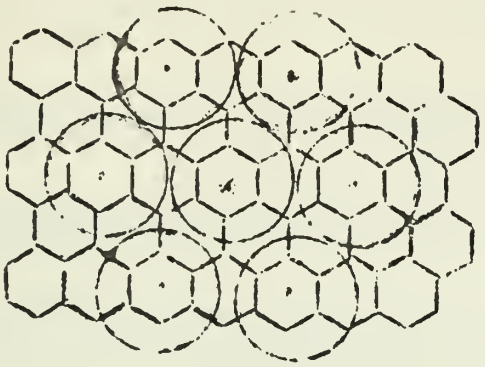
The lamellar nature of graphite gives rise to the formation of many "compounds" termed "inclusion", "insertion", "intercalation", "lamellar", or "interstitial" by various authors. Types of materials that have been inserted between graphite planes include the following: alkali metals; oxygen; halogens; and a host of compound bodies. These insertions are accompanied by a corresponding swelling of the graphite lattice, with interplanar distances increasing accordingly.

Oxygen was the first element that was fixed in the lattice of graphite. In 1855, Brodie (4) obtained a bright yellow compound by treating graphite with a mixture of $KClO_3$ and fuming HNO_3. The compound corresponds to the composition $C_{11}O_4H_5$. It turns litmus red and fixes small quantities of base, hence the name graphitic acid (also graphitic oxide).

Fredenhagen and Cadenbach in 1926 (2) were the first to report the apparently stoichiometric compounds KC_8 and KC_{16}. Since that time all of the alkali metals have been "inserted", but, as reported by Herold (4, 4a), sodium forms a much less stable compound than does Rb or Cs; lithium forms a compound differing distinctly from the Na, Rb and Cs compounds.

Rüdorf and Schulze (5) have suggested a series of "ideal" compositions for the alkali-graphite compounds: C_8M, $C_{12}M$, $C_{24}M$, $C_{36}M$, $C_{48}M$ and $C_{60}M$. The C_8M composition may be represented

nicely by interposing the metal atoms between alternate layers of graphite.



- M atom

The C_{12} composition is pictures merely by removal of the central starred metal atom to give an hexagonal structure rather than a triangular one. Successive compounds can be suggested as having 2,3 or more carbon layers interposed between metal layers. X-ray data confirm these structures.

In addition to molecular inclusion compounds described earlier ($FeCl_3$, CrO_2Cl_2, CrO_2F_2) Croft (6) reports a wide selection of intercalated compounds. (Croft defines non-intercalation to mean that less than 0.5% of the substance is detectable in subsequent analysis). He finds good correlation between paramagnetism and the extent to which various salts form intercalated structures. The following are a few of the compounds listed: $CuBr_2$, $PtCl_4$, $CuCl_2$, CuS, FeS_2, V_2S_5, Sb_2S_5, MoO_3, $AuCl_3$, BCl_3, $AlBr_3$, $GaCl_3$, $InCl_3$, $ZnCl_4$, $HfCl_4$.

Rüdorff and Hoffmann (7) have prepared graphitic salts by treatment of graphite with strong acids in the presence of various oxidizing agents. Typical of these compounds is the steel-blue colored sulfuric acid compound, $C_{24}(HSO_4)2(H_2SO_4)$. Analogous compounds can be prepared from $HClO_4$, H_2SeO_4, HNO_3 (and less easily from H_3PO_4, H_3AsO_4, $H_2S_2O_7$). All of these compounds are stable only in the presence of concentrated acid; decomposition occurs on the addition of water.

The halogen-graphite compounds vary in stability (4). Graphite takes up bromine to give a product maximum limiting ratio of C:Br = 7:1. Herold, in contradiction to Hennig, finds only adsorption phenomena taking place between graphite and chlorine. Although, it is generally agreed that iodine does not form compounds with graphite, Hennig reports the inclusion of ICl. Fluorine is known to react with graphite to yield compounds of the composition C_4F or CF (white and gray respectively) both of which explode when heated strongly, yielding gaseous fluorides and pulverized graphite (8)

Insertion is rendered possible by the lamellar structure of graphite and conditioned by the dimensions of the carbon hexagons (4). Geometric considerations of the inserted constituent are also of great importance; however, other factors related to the non-saturation of the carbon atoms must be included. The availability of electrons of graphite varies with the dimensions and chemical properties of the bodies which are inserted.

Reversibility of insertion permits the categorization of inserted substances (4).

a.) Reversible: alkali-graphite, (except Li), bromine-graphite, and the majority of combinations with compound bodies.

b.) Irreversible: graphite-Li, residual compound of graphite-Br, graphitic oxide, graphite-F.

Measurements other than reversibility lending themselves to the discovery of bonding forces are density, electrical conductivity, and magnetic susceptibility (4,9,10).

For both electronegative and metallic elements, reversible insertion requires a large atomic radius. In the case of metals, reversible insertion should be due to bonds of the metallic type, and irreversible insertion to those bonds of the ionic type. With the electronegative elements, however, irreversible insertion is due to formation of covalent bonds rather than ionic bonds. Because of their sufficiently large size compounds are not bound to a single carbon atom and thus give insertions of a more reversible type. Croft finds a good correlation between paramagnetism and successful intercalation; however Herold points out that paramagnetism is neither a necessary nor a sufficient condition for insertion (4).

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THE MAGNETO-OPTIC METHOD

Bennie A. Ferrone December 6, 1955

In 1845, Faraday noted that when a transparent, isotropic substance is placed in a strong magnetic field, that substance acquires the ability to rotate the plane of polarization of polarized light. Subsequent studies of the phenomenon by Allison[1] and Allison and Murphy[2] showed that this phenomenon is not coincident with the application of the magnetic field, i.e., there is a time lag. The magneto-optic method developed from this observation.

Experimental studies by Allison and co-workers showed that the time lags for solutions of different substances were characteristic of those substances. These time lags were manifested as minima in light intensity. The most interesting feature of the instrument was its ability to detect concentrations of substances on the order of one part in 10^{11} parts. The time lag was furthermore found to be related in some way to the chemical equivalent of the material being analyzed.

Not too many years after the results of Allison and others began appearing in the literature, a controversy developed regarding the reliability and validity of the magneto-optic method. The magneto-optic method fell into disrepute; no articles have appeared in American journals concerning it since 1939.

Experimental Results Favoring the Magneto-Optic Method

1. Evidence for the existence of heavy hydrogen[2,3] one year before its separation by Urey, Brickwedde, and Murphy[4].
2. Evidence for the presence of element 87 in nature[5,6].
3. Evidence for the presence of element 85 in nature[3].
4. Evidence for additional isotopes of Pb and Ba[7].

Arguments Against the Magneto-Optic Procedure.

1. Other scientists could not reproduce the results of Allison[8,9,10,11,12]
2. Other investigators claimed that the observed minima were due to physiological and psychological factors[13,14,15]
3. The results of the magneto-optic method conflict directly with modern theories of electrolytes in dilute solution.

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THE CHEMISTRY OF LATTICE DEFECTS

A.R. Pitochelli

December 13, 1955

The problem of defect lattices was posed nearly forty years ago when it was ascertained that there existed compounds of variable composition, like UO_2---$UO_{2.3}$. In 1930, Schottky and Wagner [1] expounded certain mechanisms for the formation of defects in crystalline lattices, but it is only in the last five years that better understanding of the fundamentals involved has developed a consequence of increased activity in the field.

A number of authors[2,3,4] have classified defect lattices into three major types: macroscopic, atomic, and electronic. Each of these may be further subdivided as follows:

1. Macroscopic
   a. Dislocations resulting from tensions exerted on solidifying or cooling
   b. Dislocations resulting from the evaporation of a solution.

2. Atomic
   a. Physical defects
      1. Schottky defects
      2. Frenkel defects
   b. Chemical defects
      1. Solid solutions in a metallic lattice
      2. Solid solutions in an ionic crystal
      3. Solid solutions formed from two semiconductors

3. Electronic
   a. Defects produced by γ-rays, u.v.rays, x-rays, and neutron bombardment.

The problem of appropriate symbolism is an important one. Rees[3] has suggested what appears to be a good system.

Energetic interpretation of the characteristics of defect lattices has contributed to an understanding of them.[3,5] Rohmer[2] points out that the usual energy level diagram where energy levels are represented by single lines is inadequate when one is considering an atom closely packed in a lattice. He suggests that a band encompassing a range of energies more closely illustrates the situation.

A number of physical methods may be used to study lattice defects. Among them are conductivity measurements[6], measurement of Hertzien absorption[7,8] and ultraviolet absorption, x-ray diffraction, density measurements, photoconductivity, and paramagnetism.

Applications of lattice defects have yielded both theoretical and practical results. Among these are the interpretation of conductivity in solids with application to semiconductors (transistors), the interpretation of the phenomenon of luminescence (oscilliscope screens, radar screens, television screens), the interpretation of photoconductivity, the interpretation of colored F-centers, a new theory for the formation of the photographic image[4,5] and the interpretation of the properties of very pure metals[9].

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THE CHEMISTRY OF QUADRIVALENT GERMANIUM.

Thet San

December 20, 1955

Cryoscopic measurements with aqueous solutions of germanium dioxide give the normal molecular freezing point depression. This led Roth and Schwartz[1] to conclude that Germanium-dioxide in aqueous solution exists almost completely in the non condensed form, H_2GeO_3. Dialysis experiments of Schwarz and Huf[2] indicated the presence of monogermanic acid below pH 5.5, of increasing amount of pentagermanic acid between pH 5.5 and 8.4 and of monogermanate ion above pH 12.5

Carpeni and Tchakirian[3] found the pH titration curves, with alkali, of germanium dioxide solutions of various concentrations, to intersect at a point, which they named the isohydric point. The results were interpreted as indicating the presence of the pentagermanate ion in the pH range 8.8 - 9.2, which is in the region of the isohydric point. They also found[4] that when the titration was carried out in the presence of 2M KCl, a white precipitate of $K_2Ge_5O_{11}$ is obtained. Souchay and Teyssedre[5] held the view that the equilibrium in aqueous solutions of germanium dioxide

$$5H_2GeO_3 \rightleftharpoons Ge_5O_{11}^{--} + H_2O \quad 2H^+$$

is displaced well to the left. With rise in pH polymerization to the pentagermanate ion first takes place; further rise in pH brings about depolymerization to monogermanate.

Everest and Salmon[6,7] observed that germanium is adsorbed by the strongly basic anion exchanger Amberlite I.R.A.-400, (in the hydroxide and chloride form) from solutions with pH values in the range 4-13, even in the presence of comparable concentrations of chloride. The results of the experiments are represented in Figure 1.

In all three cases where different concentrations of chlorides are present (curves a,b, and c) the adsorption of germanium passes through a maximum at pH of 9.0 to 9.2, whereas the adsorption of chloride is a minimum at this point (curve d). On either side of this maximum point the rapid decrease in the adsorption of germanium is accompanied by a marked increase in the adsorption of chloride. As will be seen subsequently the species adsorbed at this point is the pentagermanate ion.

In Figure 1, the amount of germanium adsorbed is given as moles of germanium adsorbed per equivalent of resin. Hence the number of germanium atoms present in one equivalent of the germanate ion adsorbed (=R) may be found in the following ways.

(a) R = (moles of Ge adsorbed)/(1 - equiv. of other species adsorbed)

(b) R = (moles of Ge adsorbed)/(equiv. of Cl in solution at equilibrium)

This method is applicable only when the chloride form of the resin is used, with no other chloride added.

(c) The resin is washed completely free of germanium so that the resin site vacated by the germanium is taken up by the hydroxide group. The hydroxide is determined by passing an excess of 0.5N sodium chloride solution through the column and determining the alkali liberated in the effluent.

R = (moles of Ge adsorbed)/(equiv. of alkali)

The values of R given in the Tables I and II, indicate that below pH 9 a lower polymer than the pentagermanate ion is adsorbed. It is believed that this lower polymer is the monogermanate $HGeO_3^-$(R=1). R = 2.5 for pentagermanate. It is also evident that above pH 11 a less complex species is being adsorbed. This is believed to be GeO_3^{2-}(R=2). This is in accord with the view of Souchay and Tevssedre cited above. From Figure I and the tables it is also evident that the monogermanic species are less readily adsorbed by the resin and more easily displaced by chloride ions. Thus the value of R for a given pH increases as the concentration of chloride in the solution is increased.

Everest and Salmon also carried out anion exchange studies of germanium solution containing sulphate and orthophosphate. The results of these experiments could be explained satisfactorily only by assuming that the complexes $[GeO_2(SO_4)]^{2-}$ or $[HGeO_2(PO_4)]^{2-}$ were also adsorbed in addition to the sorption of mono- or pentagermanate. It should be noted that the formation of these new complexes takes place in the same pH range as the polymerization of monogermanate to the pentagermanate. Thus monogermanic acid can condense with other oxy-anion as well as with itself. The formation of these new complexes throws new light on the chemistry of quadrivalent germanium.

Table I

The number of germanium atoms present in one equivalent of the germanate ions adsorbed.
(1)

pH	R	Method	pH	R	Method	pH	R	Method
I.R.A.-400-(OH); 1.8m moles of Ge, 0-0.3 m mole of Cl								
4.24	0.58	a	9.36	2.69	a	10.22	2.02	a
5.56	1.69	a	9.41	2.59	a	10.37	1.77	a
7.45	2.03	a	9.93	2.10	a	11.03	1.00	a
8.68	2.06	a						

(2)

I.R.A. - 400 - (Cl), 1.8m moles of Ge, 1.8m moles of Cl.

6.92	2.69	a	9.12	2.44	a	11.28	0.57	a
7.52	2.68	a	9.34	2.53	a	11.96	0.61	a
7.74	2.66	a	9.66	2.11	a	12.34	0.68	a
8.38	2.73	a	10.08	2.09	a	12.60	0.49	a
8.38	2.57	a	10.42	1.77	a	12.89	0.39	a

Table II

Sorption of Ge from solution (75 ml) containing 1.5m moles of Ge by I.R.A. - 400- Cl (0.25 g.) with 3.7m moles of total chloride present.

pH	R	Method	pH	R	Method
4.54	0.57	a	7.64	2.35	a
6.00	1.60	a		2.57	b
6.64	2.36	a	8.64	2.74	a
				2.54	b

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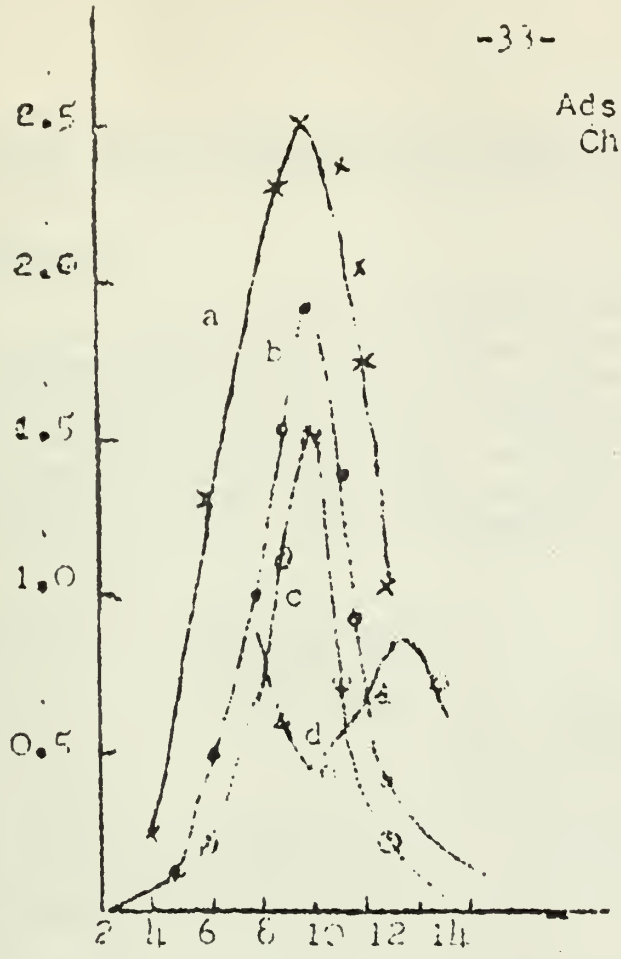
Adsorption of Germanium and Chloride by I.R.A. - 400



M moles added Ge.	Cl.	Resin form	Adsorbed on resin Ge	Cl
1.6 - 1.8	0 - 0.3	OH	x a	--
1.6 - 1.8	0.8 - 1.0	Cl	• b	--
1.6 - 1.8	1.8	Cl	o c	Δ d

SOME METAL COMPOUNDS CONTAINING THE NITROSYL GROUP

Rita M. Uznanski February 21, 1956

Among the radicals NO is almost unique, in that it can exist in three forms, namely, NO, NO^+ and NO^-. (Only I, H, NO_2 and ClO_2 behave in a similar fashion.) This gives the NO group several possibilities in regard to bond formation in various compounds. With nitrogen as the donor atom, either two electrons can be donated to the metal, or a decrease or increase of one unit charge on the metal can take place. These changes can be summarized as follows (1):

Type of Bond	Electronic Configuration	Nature of Bonding	Examples
1) M ← NO	M ⁸N⁸ ::O:	Pair of electrons donated to metal atom	A few metallic coordination complexes
2) $\bar{M} \leftarrow \overset{+}{N} \equiv \bar{O}$ resonating with $\overset{+}{M} = \bar{N} = O$	M^{x}_{o} $^{o}_{o}N^{o}_{o}$ :: $\dot{O}^{\bullet}$ $\overset{+x}{M}_{o}$ $^{o}_{o}\bar{N}^{o}_{o}$:$\dot{O}$::	three electrons donated to metal	metal nitrosyls metal nitrosyl carbonyls most coordination complexes
3) $\overset{+}{M} \leftarrow N = \bar{O}$	$\overset{+}{M}$ $^{oo}_{x}N^{o}_{o}$:$\dot{O}$: $^{-}$	electron pair bond, but also one electron donated by metal to the NO group	a few metallic coordination complexes

Most of the NO compounds fall into the second category. Of the elements investigated, the following have been found to give complexes of this type:

V	Cr	Mn	Fe	Co	Ni	Cu
	Mo		Os		Pd	
			Ru		Pt	

This list is by no means complete, since it is believed that further research will reveal other metals which are capable of similar combination.

Let us consider some of the more recent advances in the study of some compounds of iron, cobalt, ruthenium, molybdenum and nickel.

Hieber, Nast and Proeschel(6) worked with the cyano nickel complexes. They studied the reaction between potassium tricyano nickelate(I), $K_2[Ni(CN)_3]$ and NO, isolated the product from liquid

ammonia as well as from absolute alcohol and identified it as potassium nitrosyltricyano nickelate, $K_2[Ni(CN)_3NO]$. The decomposition of this product as well as that of $Na_2[Fe(CN)_5NO]$ with dilute acids was quantitatively followed.

Following this work, Hieber and his associates(7) found that hydroxylamine could be used to introduce the NO group into a complex. They proposed the following disproportionation mechanism to explain the reaction:

1) $2NH_2OH \rightarrow NH_3 + HN(OH)_2$

2) $HN(OH)_2 \rightarrow H\text{-}N{=}O + H_2O$

3) $HNO + OH^- \rightarrow NO^- + H_2O$

4) $[Ni(CN)_4]^{-2} + NO^- \rightarrow [Ni(CN)_3NO]^{-2} + CN^-$

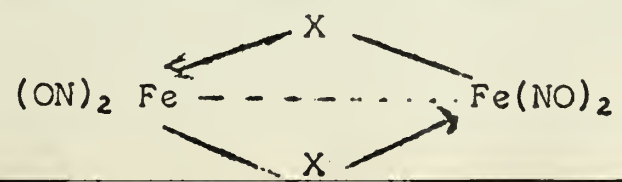
They were able to establish, by means of absorption data, that the product obtained from potassium tetracyano nickelate(II) and hydroxylamine is identical with the compound prepared from potassium tricyano nickelate(I) and nitric oxide. The analogous iron and manganese compounds were prepared in the same way.

Hieber, Nast and Gehring(5) studied the reaction of molybdenum, potassium cyanide and hydroxylamine, which leads to the formation of $K_4[Mo(CN)_5NO]\cdot 2H_2O$. This reaction also depends upon the disproportionation of hydroxylamine. That this compound doesn't have the formula $MoO_2\cdot 4KCN\cdot NH_2OH\cdot H_2O$, as had been held earlier, was confirmed by determining the amount of cyanide in it. The nitric oxide content was ascertained by the use of oxidizing agents.

Gleu and Büddecker(4) prepared the insoluble sulfate-persulfate of ruthenium(III), $[Ru(NH_3)_5NO]^{SO_4}_{(S_2O_8)_{1/2}}$, and from it the chloride, bromide, acid sulfate and neutral sulfate. These salts are stable to acids and are not reduced or oxidized, except by agents which would normally attack the NO group. In alkaline solutions, however, one mole of NH_3 is split out easily. As might be predicted, magnetic measurements showed that the sulfate-persulfate, chloride and bromide were diamagnetic.

Turning to a slightly different type of nitrosyl compound, we find that Malatesta and Sacco(8) prepared the aryl isonitrile-nitrosyl compounds, $Fe(NO)_2(CNR)_2$ and $Co(NC)(CNR)_3$. These were found to be very stable and could easily be purified by recrystallization from organic solvents.

In an attempt to explain the diamagnetism of these compounds, Ewens(2) proposed the following structure:



Each NO group contributes three electrons to the metal atom. Each iron also gains three electrons from the two bridging groups (X) and one from the Fe-Fe link, giving an E.A.N. of

$$26 + (2 \times 3) + 3 + 1 = 36$$

Short (9) made vibrational frequency studies of bonds in the nitroso-pentammine cobalt complexes, while Ghosh and Ray(3) studied the magnetic susceptibility of the black and red isomeric forms of this compound. That the red complex was diamagnetic, as had been previously determined, was confirmed by their results. The black form was found to be paramagnetic. Pauling's structure of the NO molecule containing a three electron bond was used as the basis for suggesting that the black form is an equilibrium mixture of the normal and excited states of the Co(II) complex:

$$[(H_3N)_5 \cdot Co \; {}^{\cdot}N \overset{\cdot\cdot}{=} O \;]^{++}$$

The spins of the promoted electron may be either parallel or anti-parallel to that of the odd electron in the three electron bond of the NO molecule, representing the normal and excited state of the molecule, respectively. The former corresponds to the paramagnetic state and the latter to the diamagnetic one.

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THE NITRIDES, CARBIDES, BORIDES AND SILICIDES OF THE TRANSITION METALS[1]

John W. Pankey February 28, 1956

The nitrides, carbides, borides and silicides of the transition metals have been the subject of many scientific and technical studies in recent years. The physical properties of these compounds are of great significance because many of these properties are a combination of the properties of the pure metals with the properties of the high melting oxides. Consequently, compounds with these properties are finding many new uses.

The compositions of the compounds are not determined by the usual valence restrictions of the components. The crystal lattice is determined by the more metallic atoms, the smaller metalloid atoms being taken into this lattice principally in the atomic state. If the ratio of the atomic radius of the metalloid to the atomic radius of the metal does not exceed 0.59 a very simple crystal structure results.[2] If the ratio exceeds 0.59, the simple lattice is expanded too greatly, the simple lattice breaks down, complicated crystal types result and there is a loss of metallic properties. The compounds in most cases can be prepared by direct synthesis.

With the exception of those transition metals with the smallest atomic radii all transition metal nitride structures are simple. Many nitrides are isostructural with the corresponding carbides.

The carbides of Groups IV, V and VI are all typical hard, metallic compounds. The other transition groups are somewhat more complicated.

The boride systems are all fairly complicated due to formation of boride chains. The properties of the borides are similar to the properties of the nitrides and carbides. The properties of the silicides are also similar to those of the nitrides, carbides and borides. However, true entrapment structures for the silicides are not to be expected. The silicides are diamagnetic whereas most of the nitrides, carbides and borides are paramagnetic.

Studies of ternary systems have been made of systems with two different transition metals to one metalloid and with one transition to two different metalloids.

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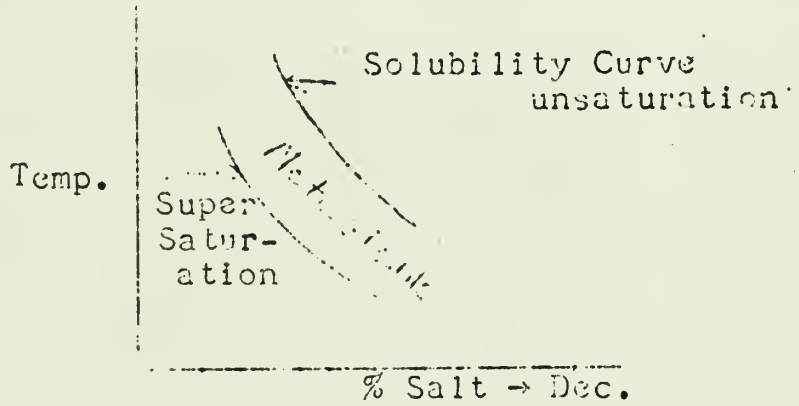
NUCLEATION AND CRYSTAL GROWTH

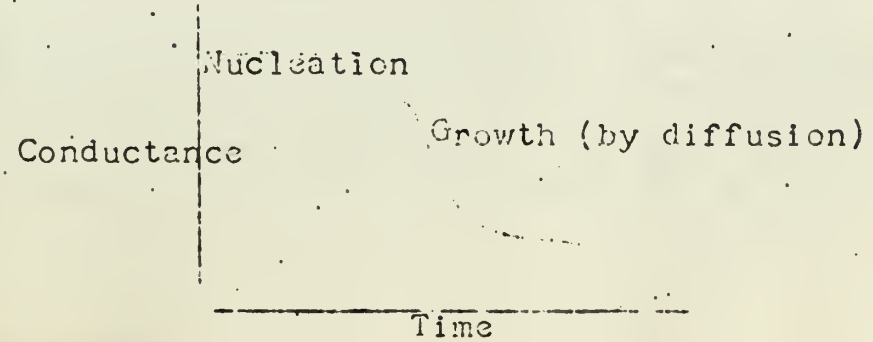
Benjamin Mosier March 6, 1956

Throughout the 19th century much interest was shown in crystallization of supersaturated solutions, e.g. salt, $MgSO_4$, vitriols, etc. Boishaudron found that crystallizati takes place only in strongly supersaturated solutions, and de Coppet[2] by cooling solutions, determined the limits of solubility at which spontaneous crystallization begins. Osterwa developed the idea of the metastable zone on the solubility diagram, showing the limits at which no crystal nuclei could form.



Tammann's[4,5] work on the initiation of crystallization in undercooled organic liquids and inorganic glasses was of great significance. By making counts of nuclei under controlled conditions he showed that the formation of nuclei obeyed the laws of probability and that maximum probability occurred at temperatures 40 - 120° below the melting point, where the liquids begin to lose their mobility and show marked changes in viscosity. Tammann also stated that there is a metastable zone a few tenths of a degree below the melting point. Tammann considered that since the formation of a nucleus was a rare event, a large number of molecules must meet under limiting conditions of velocity, orientation and direction of movement before a nucleus can be formed.

Johnson and O'Roarke[6] have shown by conductance measurements that there is a nucleation period and growth period. After a certain period of time we will have no new nuclei formed and then growth by diffusion takes over.



Von Weimarn[7] studied the size of crystal particles as a function of time. Von Weimarn postulated several empirical rules and showed that (1) growth depends upon time, (2) with increasing concentration the size of the crystal decreases, (dilute solutions were, however, overlooked) (3) as the particle size decreases the solubility increases.

Certain facts of crystal growth have been observed with sufficient regularity to be regarded as general principles. For example, it has been shown that (1) growth rate increases with increasing supersaturation and with agitation (2) different faces of a single crystal grow at different rates (3) flawed surfaces grow more rapidly than corresponding surfaces without detectable flaws (4) the crystal growth rate in solution increases with increasing temperature.

In general in aqueous systems compounds which grow readily are quite soluble. Slightly soluble compounds are generally grown with great difficulty and highly soluble compounds are grown with great ease. It has also been shown that ease of growth increases with increasing association of the solute. HIO_3 is typical of compounds known to be highly associated. Nuclei form only with considerable supersaturation, and large perfect crystals are easily grown. NaCl is a typical example of a compound which is soluble but highly dissociated in solution, and experience indicates that NaCl is virtually impossible to grow into a perfect crystal at any reasonable rate from pure solution. It forms coprous nuclei with small degrees of supersaturation.

Crystals in general, grow by the spreading of discrete layers one after the other across the face of the crystal. Bunn and Emmett have shown that when a succession of thin layers of ionic or molecular thickness spreads across a crystal face, the surface is not a surface of high index but a face of very high index. Faces of high indices are less stable and presumably have a higher surface energy than those of low indices.

Growing Single Crystals

When, as customarily, the solubility of the salt to be crystallized, increas es with temperature, it is more satisfactory because more readily controllable, to grow crystals by slowly cooling the solution than by evaporating it. Rough rules to guide a preliminary experiment are: (1) salts in the solubility range of 20 to 50 weight percent (or about 5-10 mole percent) will tolerate a linear advance of the fastest growing faces of 0.05" to 0.10" per day, and (2) the lower the solubility, the lower the tolerable rate.

There are four principle methods of growing metallic single crystals: solidification from the melt in a vacuum; electrodeposition; condensation and decomposition from the vapor; and the strain and anneal method. The crystals of most of the common metals can be grown by solidification from the melt.

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[illegible] OF [illegible]

W. Kenneth Musker

March 13, 1956

Interhalogen compounds have been known for more than 100 years and at present eleven such compounds are known (1). These are tabulated below.

Type AX	Type AX_3	AX_5	AX_7
ClF	ClF_3	BrF_5	IF_7
BrF	BrF_3	IF_5	
BrCl	ICl_3		
ICl			
IBr			

No ternary interhalogen compounds are known at the present time. You will note the absence of a binary IF compound (1). Only the fluorides of the hepta- and pentavalent halogens are known and iodine is the only halogen which has a covalency of seven (1). The preparation of these interhalogen compounds is usually done by the direct union of the elements (5) (1)(5); the only exception being that of IF_7. Some physical properties of the interhalogens are discussed by Sidgwick (6). It is interesting to note that all of the known interhalogen compounds and polyhalides contain odd numbers of halogens or even numbers of electrons. (2)

Halogen fluorides are used as powerful fluorinating agents. The order of reactivity of the fluorides is given by the following list of compounds $ClF_3 > BrF_5 > IF_7 > ClF > BrF > IF_5 > IF_7$ (10). These fluorides react with metals and thus to oxidize them to their highest oxidation states.

Iodine chlorides and iodine bromides have been investigated slightly (7)(8). ICl is polymorphous, existing in two forms (9). In some solvents ICl exists as a dimer with the formula I_2Cl_2, but IBr forms no dimer. Both ICl and IBr ionize in non-polar solvents.

$$2IX \rightarrow I^+ + IX_2^-$$

Bladky and Thor (8) studied the ionization of the IY-IX and ICl_3-IX systems.

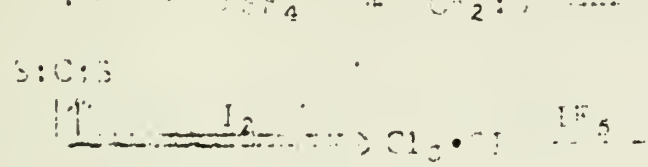
ICl_3 has been used in forming polyhalogen cations of the type ICl_2^+. ICl_3 ionizes in acetic acid to give ICl_2^+ and $(CH_3CO_2H)_n^{++}$ or ICl_2^+ and ICl_4^-, the latter being the most probable. (10)

The structure of the ICl_4^- ion is linear with the extra electrons above and below the plane of the chlorine (1). ICl_3 exists in the dimeric form, I_2Cl_6, as determined by crystallographic studies.

ClF and BrF_3 have been investigated (12)(13)(14)(11)(25) because they are very powerful fluorinating agents and they have a good liquid range. (ClF -830 to +12°) and BrF_3 +9 to +1270)(1). They react with metals and non-metal oxides forming fluorides and also with alkali metal fluorides to form complexes. They have also been used in the fluorination of organic molecules. BrF_3 forms salts of the type BrF_2MnF_4 and BrF_4. IF_5 can be prepared by a

typical acid-base type reaction: $BrF_2SbF_6 + KBrF_4 \rightarrow KSbF_6 + 2BrF_3$.

IF_5 has not been investigated as much as the trifluorides. One series of reactions is interesting (15) for it postulates the existence of IF_7 as a possible intermediate.



IF_5 and ClF_3 are said to form a compound for when they are mixed the mixture heated above 120°C, the ClF_3 does not boil off. No speculation was made as to its composition if any compound is formed. Instead of being a trigonal bipyramid as first postulated(2), the structure of the IF_5 molecule is a square pyramid with the four odd-fluorine atoms on the fourth axis normal to the plane (3). IF_5 is used as a fluorinating agent in reactions with $COCl_2$ and CS_2. It can also be used in preparing HgF_2 (16).

The structure of IF_7 has been compared to that of Al_2Cl_6 (17) as shown by the formula $F_6I \cdot F \cdot IF_5$ but it is probably a pentagonal bipyramid (18).

The chemistries of BrF, BrCl, ClF, and BrI_3 have not been discussed in the literature; only the proper names and physical constants are given. (1)(6)

Polyhalides have been divided into three classes X_2^-, XX'_n^-, and $XX'X''^-$ (2). The best known polyhalide ion is I_3^- but both I_5^+ and some interhalogen compounds CsI_3, KIF_6, and $NiCl_3$ can be formed. The structure of the polyhalide ICl_2^- is a trigonal bipyramid. Polyhalides are ionic, decomposing in non-polar solvents.

More information about polyhalides is given by Duncan and Cremar (20-24).

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THE OXIDATION OF FERROUS ION BY AIR

M. L. Judd March 20, 1956

This topic is of special interest because of the many discrepancies found in the literature concerning it. Ferrous salts are reputed to be easily oxidized on exposure to air and text-books of analytical chemistry prescribe elaborate precautions for the exclusion of air in making up standard solutions of ferrous salts. In point of fact, however, acid solutions of ferrous salts are not easily oxidized. Much of the confusion on this matter arises from the effect of various reagents on the rate of oxidation. This is illustrated in the following table in which the numbers indicate the number of papers found which report the indicated effect on the rate of oxidation of ferrous ion.

Reagent	Increase	Decrease	No Effect
Cu(II)	4	1	1
Zn(II)	1	1	
Mn(II)		1	1
Ni(II)		1	1
H_2SO_4		5	1
Increasing Fe(II) concentration	2	4*	

* This is dependent upon the catalytic mechanism involved.

The bulk of the evidence indicates that copper(II) ions, nitric oxide, charcoal, platinum and complexing anions such as oxalate, citrate, lactate and gluconate accelerate the aerial oxidation of ferrous ion while sulfuric acid retards it.

Several mechanisms by which the oxidation may take place have been proposed. Jander (1) favors a two step process consisting of a slow primary reaction,

$$2FeO + O_2 + H_2O \rightarrow Fe_2O_3 + H_2O_2$$

followed by a rapid reaction.

$$2FeO + H_2O_2 \rightarrow Fe_2O_3 + H_2O$$

The postulation of Fe^{++} as the oxidizeable species is compatible with the retarding action of sulfuric acid on the oxidation rate. Mikhelson (2) has expressed similar views. A. B. Lamb and Elder (3) doubt this mechanism on the basis of the catalytic activity of the copper(II) ion on the system. A step wise mechanism is suggested by Manchot and Schmid (4). According to them, the first step of the process involves a loose union between the oxygen and ferrous oxide (eg. $(FeO)_2 \cdot O_2$). This intermediate then splits out an activated oxygen atom leaving the oxidized form of the iron.

$$(FeO)_2 \cdot O_2 \rightarrow Fe_2O_3 + [O]$$

The activated oxygen atom is then free to oxidize more ferrous ion or combine with another oxygen atom. E. Abel (5) believes the kinetics of the reaction to be best explained by a series of steps:

1.) $O_2 + O^{-2} \rightarrow O_2^- + O^-$
2.) $O_2 + OH^- \rightarrow O_2^- + OH$
3.) $Fe(II) + O_2^- \rightarrow Fe(III) + 2O^-$
4.) $Fe(II) + OH \rightarrow Fe(III) + OH^-$
5.) $Fe(II) + O_2 \rightarrow Fe(III) + O_2^-$

The catalysis may follow any one of several mechanisms. Kuzminykh and Babushkina (6) report on the catalytic activity of the copper(I) ion. "It may be concluded that this (accelerating) effect of copper on the rate of the $Fe^{++} \rightarrow Fe^{+++}$ oxidation by atmospheric oxygen is connected with the inherent variability in the valence of copper, which enables it to function in acid ferrous sulfate solutions as a Cu(I) as a carrier for dissolved oxygen to the ferrous ion." This might alternatively be considered as the oxidation of ferrous ion by copper(II) followed by the oxidation of copper(I) by oxygen.

Concerning the catalytic accelerating action of nitric oxide, Thomas and Williams (7) report that, "The mechanism of the catalytic action of nitric oxide on the oxidation of the ferrous salts by air is the oscillation of the oxide of nitrogen between two states of oxidation." Lamb and Elder propose that peroxides of the various catalysts are formed first; these either oxidize the ferrous salt directly or accomplish this same result by hastening the formation or decomposition of a peroxide of iron.

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UNFAMILIAR OXIDATION STATES OF NICKEL

J. A. Seaton March 27, 1956

The electronic configurations of the first transition series, possessing incomplete 3d orbitals, permit variable valences among the metals of this series. Nickel, however, commonly exhibits only +2 or O oxidation states. Recent investigations have shown nickel to display the oxidation states +1, +3, and +4.

Nickel(O). Nickel carbonyl has been known since 1890 (1). It is tetrahedral in structure, utilizing $4s4p^3$ bonding, and is represented by a formula with four Ni=C=O bonds (2). Most of the Ni(O) compounds are of similar structure, with the atom bonded to the nickel being one which is capable of forming a double bond with the nickel. Resonance structures are said to stabilize these compounds.

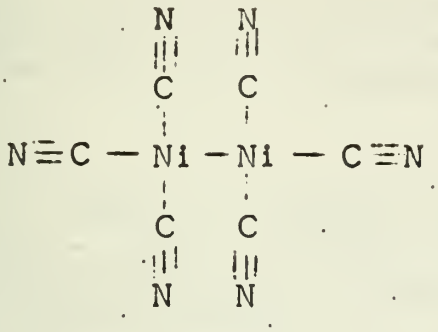
Isonitrile and alkynyl nickel(O) derivatives have been prepared, which are formulated $Ni(CN\phi)_4$ and $[Ni(C{\equiv}CH)_4]^{4-}$. The former are prepared in alkaline medium by reduction of nickel(II) compounds with hydrazine in the presence of the isonitrile (3). The alkynyl compounds are prepared by reducing $[Ni(C{\equiv}CH)_4]^{2-}$ with sodium in liquid ammonia (4) (5).

Goehring and Debo have reported the preparation of $Ni(NS)_4$, which apparently consists of four [NS] groups attached to the nickel (6).

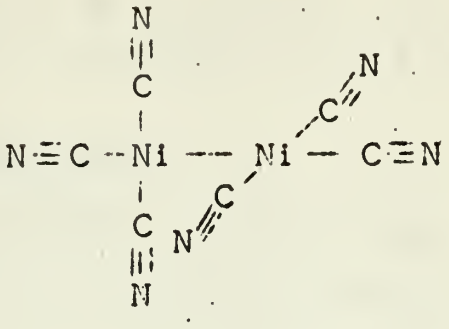
A number of nickel(O) compounds have been prepared in which substituted arsines and phosphines are used as ligands (15)(16).

Nickel(I). The structure of the compound with the empirical formula, $K_2[Ni(CN)_3]$ has been the subject of much speculation. It is diamagnetic, suggesting that it is a dimer, $K_4[Ni_2(CN)_6]$, and a preliminary X-ray investigation has shown this to be true. Furthermore, the X-ray data indicate that the compound is planar, and has a bridge-structure (7). Nast and Pfab suggest a bridge structure consisting of two $\overset{N}{\overset{\|}{C}}$ groups between the nickel atoms.

Infra-red investigations have been used to determine the structure of $K_4[Ni_2(CN)_6]$ (8). The authors consider possible structures in the light of both X-ray and infra-red data. Structures I and II were considered to be most probable, if the X-ray data could be disregarded. Structure III contains $>C=N$ linkages which were not detected in the infra-red. While structure IV fits all the data, the authors consider it to be much less energetically favored than structures I or II, which can be formed from the ground state of nickel(I). Structure IV requires the elevation of an electron to the 4p level, while structures I and II form four dsp^2 bonds about each nickel without electron promotion.



I



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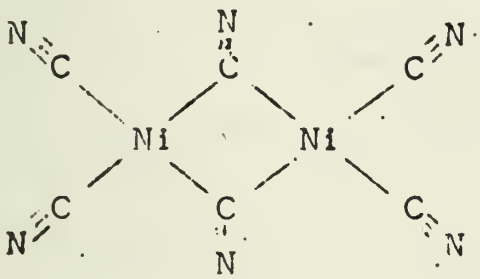
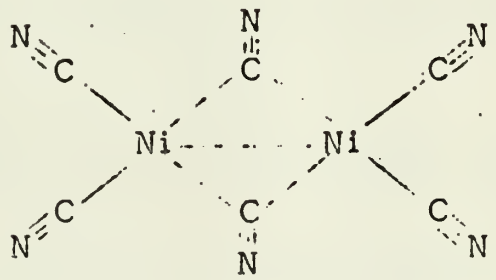


III



IV

A compound with the empirical formula $K_2[Ni(CN)_3CO]$ has been prepared in pure crystalline form by the reaction of $K_4[Ni_2(CN)_6]$ with carbon monoxide in liquid ammonia (9). The diamagnetism of this compound suggests a dimeric structure.

Nickel(III). Nyholm has studied the oxidation of bis(o-phenylenebisdimethylarsine)nickel(II) complexes to $[Ni(diars)_2X_2]X$. (10). This compound has an octahedral configuration.

Five-covalent compounds of nickel(III) with the composition $NiBr_3 \cdot 2PEt_3$ have been prepared by Jensen (11). Dipole moment studies rule out the possibility of a bipyramidal configuration for this compound and give strong evidence for the square pyramidal structure, the probable bond-type being dsp^3 or d^2sp^2.

Sodium and lithium nickelate(III) have been prepared in pure crystalline state by bubbling oxygen through melted sodium or lithium hydroxide in a nickel tube heated to 650-850°C (12). Single crystal X-ray studies were made on these compounds and Fourier projection techniques were employed to determine their structures. $LiNiO_2$ was found to be rhombohedral and to have the $CsCl_2I$ structure. $NaNiO_2$ was found to exist in two forms with a transformation temperature of 220°. The high temperature form is isomorphous with the Lithium compound, while the low temperature form is a monoclinic distortion of the $LiNiO_2$ structure. These compounds are stable when not in contact with moisture or carbon dioxide.

Nickel(IV). Nickel(IV) complexes can be formed by the reaction of Ni(II) salts of thioacids with carbon monoxide in alkaline media via disproportionation to Ni(O) and Ni(IV) (13).

The nickel(III) complex with o-phenylenebisdimethylarsine, $[Ni(diars)_2Cl_2]Cl$ can be oxidized to the corresponding nickel(IV) compound (10). This compound is diamagnetic and assumed to be of octahedral d^2sp^3 bonding.

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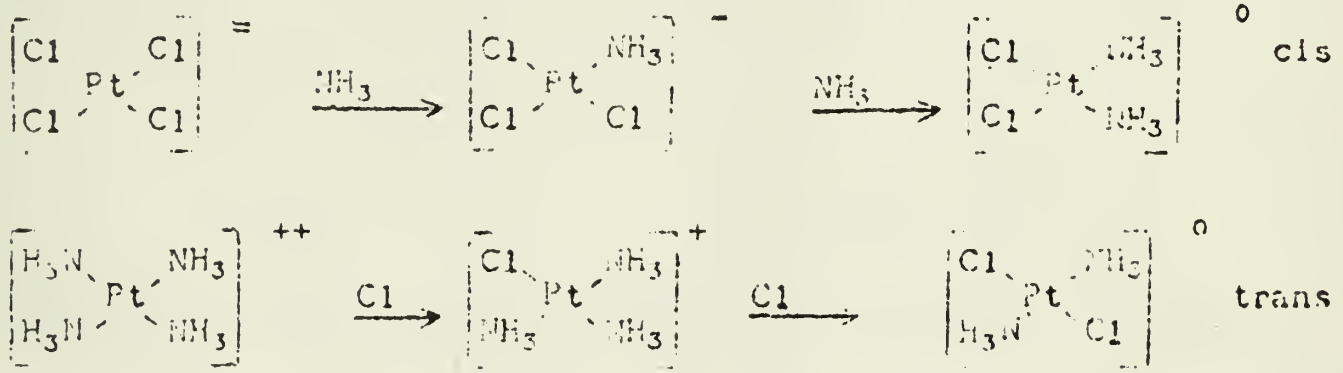
THE TRANS EFFECT

Dorian S. Smith April 10, 1956

The occurrence of directive influences in the reactions of inorganic coordination compounds was noted as early as 1893 by Werner[1]. Investigation since then has led to the observation that these guiding forces occur particularly in square planar platinum(II) compounds; similar, but weaker forces are thought to influence the course of substitution in other complex compounds, especially those of planar palladium(II) and octahedral cobalt(III), rhodium(III), and platinum(IV).

The classical reactions for the formation of dichlorodiammine platinum isomers serve to illustrate the phenomena described above[2].



Chernyaev, in 1926, proposed the term "trans effect" to describe these occurrences[3]. The "trans effect" as commonly defined stipulates that the bond holding a group trans to an electronegative or other labilizing group is weakened.

An arrangement of the common ligands of inorganic complex chemistry can be made according to their tendency to direct a second substituent into the trans-position. In approximate order of decreasing trans directing effect may be listed: $CN^- \sim C_2H_4 \sim CO \sim NO > SC(NH_2)_2 \sim R_2S \sim PR_3 \sim SO_3H^- > NO_2^- > I^- > CNS^- > Br^- > Cl^- >$ pyridine $> RNH_2 \sim NH_3 > OH^- > H_2O$.

The manner in which a ligand exerts its directing influence is not clearly understood, but it has been generally assumed that the bond in the trans position to a group possessing high trans effect is weakened. Chatt and coworkers[4,5], finding evidence that in certain cases this bond may actually be strengthened, propose the more equitable definition: "The trans-effect or trans-influence of a group (A) coordinated to a metal ion is the tendency of that group to direct an incoming substituting group into the trans-position to itself (A)."

Attempts to explain the trans effect have met with limited success because of the complexity of the problem[6]. Grinberg[7] noted that the trans effect increased in the series OH^-, Cl^-, Br^-, I^-, (i.e., in the order of increasing polarizability). In a complex $(PtX_4)^=$ where X^- is a halide ion, polarization of the anions is expected; however, due to the symmetrical distribution of the anions around the central atom, the induced dipoles of the central metal ion cancel and the resultant dipole is zero (Figure I). If a group Y of different polarizability is introduced there will be no mutual compensation and a polar central ion will result, facilitating labilization of a trans X group (Figure II). The group Y is an easily polarized group or an electron rich group such as CO, C_2H_4.

Figure I

Figure II

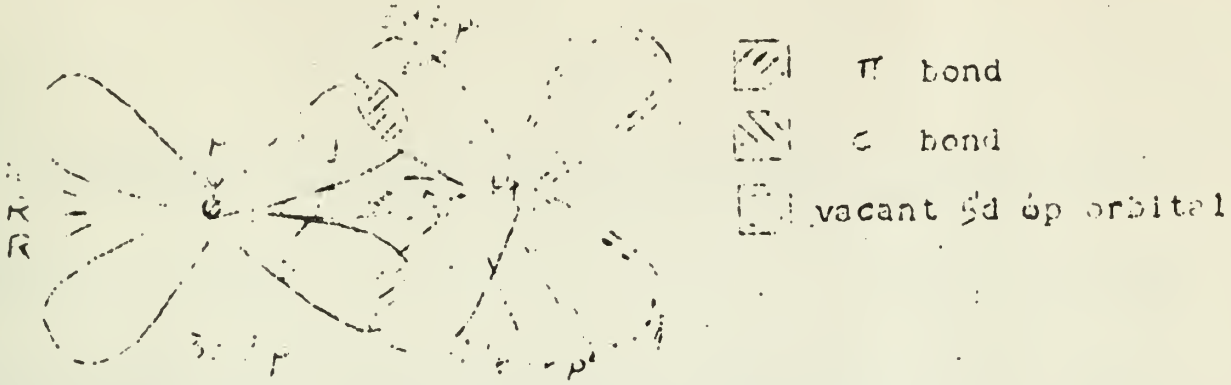
Grinberg[6], making use of field strength and polarizability data, later developed a more sophisticated treatment of the problem which corroborates the above simplification.

The relationship between covalent character and trans effect has been offered by Syrkin[9] who states that the greatest labilization occurs with groups trans to ligands with the highest degree of covalent bonding. Thus, any factors contributing to the covalent nature of the bond (such as resonance energy) can be correlated with trans labilization.

Another hypothesis is forwarded by Chatt[4] who concludes that the amount of double bonding between a metal and a ligand is the main cause of the trans effect. Utilizing atomic orbital theory, he proceeds to describe a mechanism for the trans effect.

The σ and π components of a double bond binding a ligand to a suitable transition metal may be described as follows. The σ bond is formed by donation of a lone pair of electrons from the donor atom to the metal. The π type bond (dative π bond) is formed by the overlap of a filled d or dp hybrid orbital of the metal and a vacant p, d, or dp hybrid orbital of the donor. Figure III

depicts a schematic representation of the R_3P-Pt bond



This above π bond formation is in sharp contrast to the R-N-Pt bond which has no π component due to the absence of vacant orbitals in the valency shell of nitrogen.

It is interesting to note that in F_3P=Pt and OC=Pt the bonds are almost nonpolar, indicating that the donation of electrons in the σ bond is nearly equal to the back donation in formation of the π type bond. It is readily visualized that a ligand of high double bonding capacity will withdraw d electrons from the metal atom thus increasing its electron affinity and making it more susceptible to nucleophilic attack in the trans position (Figure IV).

Figure IV

Ligand A is bound to metal M by $p_\pi d_\pi$ dative π bonding. Electron withdrawal toward A facilitates replacement of B in the trans position.

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SEPARATIONS INVOLVING CONTINUOUS PAPER ELECTROPHORESIS

Marguerite E. Conroy April 17, 1956

Electrophoresis may be defined as the migration of charged particles in the presence of an electric field. There are two types of electrophoresis: boundary electrophoresis, in which the movement and separation of boundaries is observed by optical or analytical methods, and zone electrophoresis, in which the components migrate as separate zones (1). The latter is possible only if the components are stabilized against convection by some sort of supporting medium, e.g. filter paper, starch, glass powder, silica or agar gel. Specifications which the filter paper must meet for exacting work are: even-machining, high wet strength, low electroosmosis, and chemical inertness toward the analyzed substances. Thickness of the paper varies widely according to its use.

Although the apparatus used for filter paper (zone) electrophoresis varies somewhat with the individual worker, there are three typical types: Durrum's (2)(3), with freely hanging nonhorizontal paper, Wieland's (4), with freely hanging horizontal paper, and Cremer and Tiselius' (5), with the paper between glass plates. Common features are: use of large electrode vessels to minimize the effect of electrode reactions, and construction which minimizes free evaporation to the surroundings.

Working conditions which must be considered are: temperature, buffer (kind and concentration), and potential gradient (1)(10). The paper medium in contact with the buffer is likely to behave as a charged membrane and give rise to polarization phenomena.

Continuous paper electrophoresis allows fairly large volumes of solution to be separated without the necessity of making the apparatus too bulky. Figure 1 illustrates the continuous vertical ("nonhorizontal") strip method. Buffer solution is fed evenly from the vessel along the top surface of the paper and it is evenly drained along the bottom, so that an evenly distributed vertical flow of the solution is obtained. The solution to be separated is also introduced at the top and will therefore normally flow as a narrow vertical band, emerging at one or more outlets at the bottom of the paper. When an electric current is passed through the paper horizontally, the combination of the vertical flow and the horizontal electrophoretic migration produces a zone separation. The separated fractions are collected at suitable outlets. The process is rather slow, as the apparatus must not be overloaded. Important problems are to obtain an even flow and to apply the proper electric current.

Dicastro and San Marco have devised an apparatus for continuous electrophoresis on paper which, they claim, eliminates the undesirable conditions of non-uniform electric field and differing pH concentrations throughout the paper (13).

In continuous paper "electrochromatography", which has been employed by Strain and coll. (6-9) and Lederer (12), the path taken by an ion is the resultant of its electrophoretic mobility vector and its chromatographic adsorbability vector. Differences between ions are enhanced by use of a complexing agent such as citric acid, tartaric acid or Versene. Lederer separated lanthanum and actinium, and rare earth mixtures by discontinuous (11) and continuous (12) methods using citric acid as electrolyte. It took five days to separate 3 ml. of a solution containing 30 mg. of rare earths by the continuous method, but Lederer claims that this compares favorably with ion exchange methods in speed and quantity of citric acid used. Strain et al. (8), on the other hand, used lactic acid and, less successfully, tartrate, for discontinuous electrophoretic separation of the rare earths.

Of particular interest are the numerous separations of inorganic ions by continuous paper electrophoresis which were carried out by Strain and coworkers. Mixtures of inorganic ions which were separated were: silver and copper, nickel and copper, nickel and chromate, silver and nickel, ferric and aluminum, arsenic-antimony and tin, silver-nickel-copper and ferric (6). Wash liquids employed were lactic acid, ammonia, disodium tartrate and tartaric acid. Developing reagents used to show up the paths of the ions were: dithiooxamide, diphenylthiocarbazone, dithiooxamide and lead salts, aluminon in acetic acid, and H_2S. Applied voltages were in the range 160-300 v. Currents were in the range 30 to over 100 ma. In most cases except ammonia, solutions and reagents were very dilute, 0.005M and 0.1-0.01M respectively. Increased concentration of reagent led to decreased separability.

Radioautographs were used by these workers to indicate the paths of radioactive calcium and phosphate ions in a mixture of $Ca^{45}Cl_2$ and $H_3P^{32}O_4$ (7). Radioautographs were also used to indicate the separations in the following mixtures: strontium, cerium, yttrium and phosphate; cesium, strontium, yttrium, cobalt add phosphate; and niobium, zirconium, uranium, strontium, yttrium and cesium (9). The same publication described substitution of low concentrations of mineral acids as electrolytes in the continuous method in place of the more expensive organic acids like lactic and tartaric. A mixture of silver, nickel, copper, uranium, thorium and zirconium ions was separated using nitric acid.

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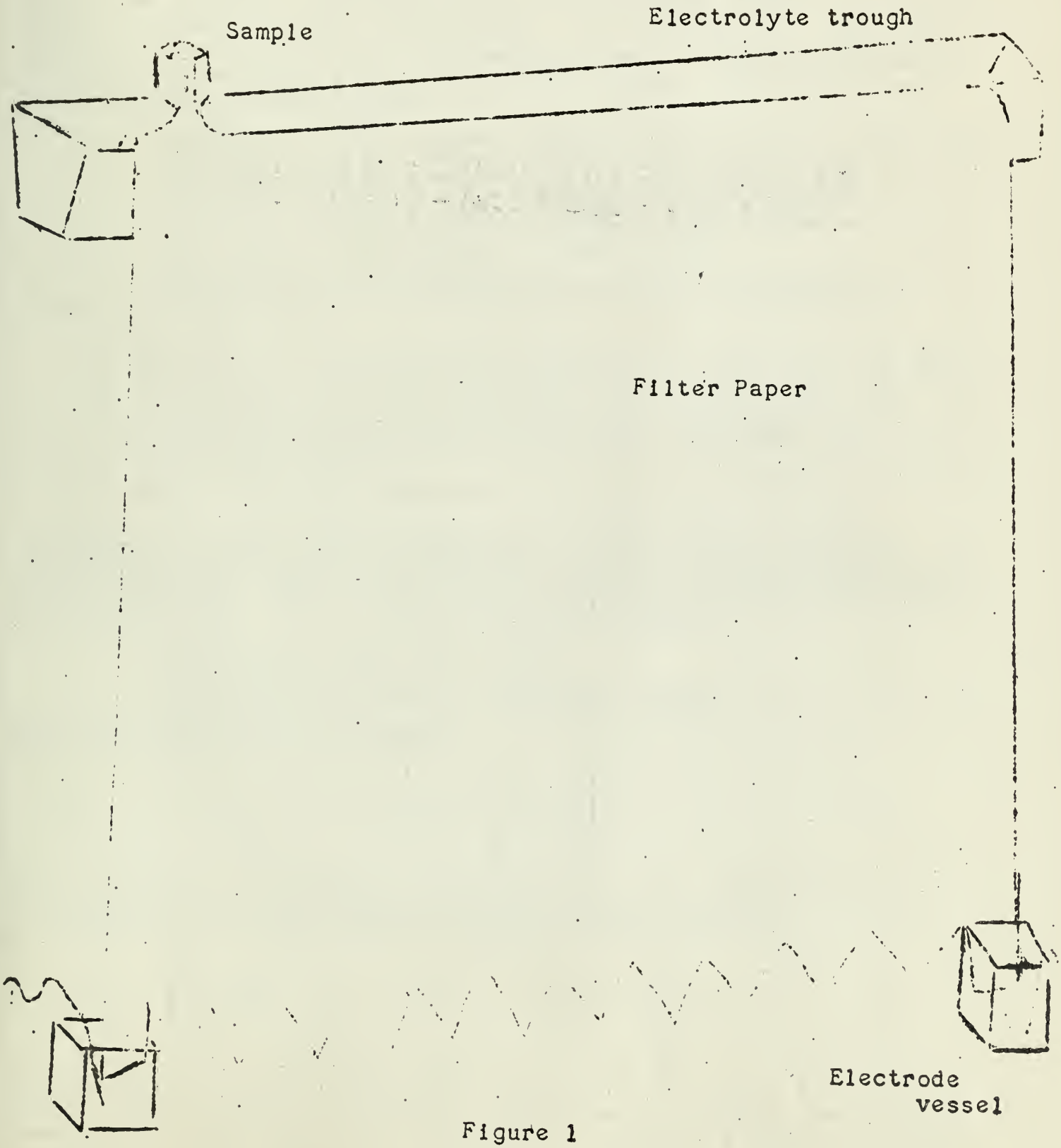


Figure 1

Apparatus used by Lederer

SOME HALOGEN COMPOUNDS OF BORON

Valentine D. Galasyn April 24, 1956

I. Although dihydroxydifluoroboric acid, $H_3BO_2F_2$, has been known for a number of years, much that is fundamental regarding its general chemical nature is unknown. In an attempt to throw some light on the structure of the monobasic acid, Long and Dollimore studied its behavior with halogenating agents. The following reactions were established:

$$3H_3BO_2F_2 + 3PX_5 \rightarrow BPO_4 + 2POX_3 + 2BF_3 + 9HX \quad (X = Cl, Br)$$
$$3H_3BO_2F_2 + 2PI_3 \rightarrow [B_2O_3 \cdot P_2O_3] + 6HI + BF_3 + 3HF$$
$$3H_3BO_2F_2 + 4SOCl_2 \rightarrow 8HCl + 4SO_2 + 2BF_3 + HBO_2$$
$$2H_3BO_2F_2 + P_2O_5 \rightarrow 2BPO_4 + [H_2O] + 4HF$$

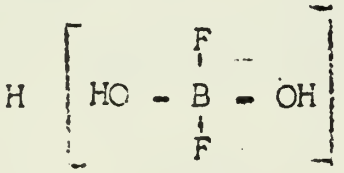
$6H_3BO_2F_2$ may alternatively be given the following "reaction formulae".

1. $B_2O_3 \cdot 4BF_3 \cdot 9H_2O$ represents the reaction with PCl_5 and PBr_5
2. $2B_2O_3 \cdot 2BF_3 \cdot 6HF \cdot 6H_2O$ represents the reaction with PI_3
3. $2HBO_2 \cdot 4BF_3 \cdot 8H_2O$ or $2H_3BO_3 \cdot 4BF_3 \cdot 6H_2O$ represents the reaction with $SOCl_2$
4. $3B_2O_3 \cdot 12HF \cdot 3H_2O$ represents the reaction with P_2O_5

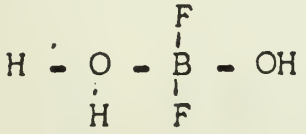
No single reaction formula accounts for the general chemical behavior, so more than one molecular species may be present in the anhydrous acid. Many of the reactions are more easily explained by assuming that the following equilibria occur:

$$3H_3BO_2F_2 \rightleftharpoons 2BF_3 \cdot 2H_2O + HBO_2$$
$$3H_3BO_2F_2 \rightleftharpoons BF_3 \cdot 2H_2O + BF_3 \cdot H_2O + H_3BO_3$$

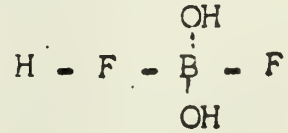
Sowa has suggested the formula



while Kroeger has suggested coordination of the acidic hydrogen to oxygen or fluorine atoms, giving molecules such as



and



However, Long and Dollimore feel that since hydrogen, fluorine, and hydroxyl groups are present, molecules of $H_3BO_2F_2$ are strongly associated. Hydrogen bond formation is strongly suggested by the physical properties of the acid (high viscosity, density, boiling point, heat of vaporization).

Since the vapor density is about half that required by the formula $H_3BO_2F_2$, Sowa has suggested that HF and $BF(OH)_2$ are present in the vapor. But the vapor does not attack glass, so an alternative

$$\underset{\text{(liquid)}}{H_3BO_2F_2} \rightleftharpoons H_2O + \underset{\text{(vapor)}}{BF_2 \cdot OH}$$

may be more probable.

II. In trying to prepare some mixed halides of boron, the partial chlorination of boiling BBr_3 by using AgCl, $HgCl_2$, and $SbCl_3$ was attempted, with the latter giving the best results. The physical behavior of the product was that of a mixture of BCl_2Br and $BClBr_2$. However, repeated fractional distillation led to progressive disproportionation, and attempts to isolate the pure compounds failed. Low temperature separation attempts were also unsuccessful, but gave clear evidence for the existence of the mixed halides as well as progressive disproportionation.

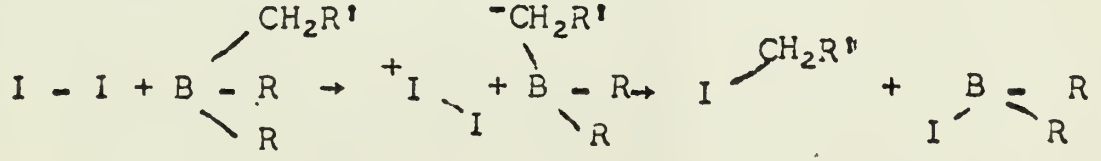
If an equilibrium of the type

$$BCl_3 + HBr_3 \rightleftharpoons BCl_2Br + BClBr_2$$

exists, it should be possible to prepare the boron chlorobromides by keeping mixtures of BCl_3 and BBr_3 at room temperature. Raman studies verify this, as well as the formation of the chlorobromides with the previous method.

III. The action of iodine on tri-n-propylborine leads to the production of di-n-propyliodoborine in fair yield, along with the slow production of the diiodoborine. A reaction mechanism was suggested to account for the formation of the mono-iodoborine, as follows:

As the trialkylborine is approached by an iodine molecule the tendency for the iodine molecule to donate an electron pair to the boron atom results in an increase in electron density on the iodine atom nearest the boron atom. If the approach is broadside the decrease in electron density around the second iodine atom will further an accumulation of negative charge on the carbon atom nearest the second iodine atom, thus favoring a so-called "switch" of electron pairing.



The introduction of the electronegative iodine atom discourages further dealkylation by a mechanism like this, but the slow formation of the diiodoborine possibly arises through disproportionation of the monoiddoborine

$$R_2BI + IBR_2 \rightleftharpoons R_2BI_2^- + BR_2^+ \rightarrow RBI_2 + BR_3$$

Evidence that disproportionation plays a role in this further

dealkylation is brought out by the difficulty in purifying the monoiodoborine.

IV. Halogen substitution was attempted on di-n-propyliodoborine by the use of antimony trihalide. The reaction was successful with bromide and chloride,

$$3BR_2I + SbX_3 \rightarrow 3BR_2X + SbI_3 \qquad (X=Cl,\ Br)$$

but was slower and followed a different course with SbF_3. In the latter case, propylborine was formed instead of the monofluoroborine.

With silver fluoride an exothermic reaction went to completion but it was very complex and led to a variety of products, seemingly due to boron-carbon and carbon-carbon bond fission.

A slight general decrease in reactivity was found with these compounds in passing from Cl→Br→I, and this is probably associated with a more pronounced steric factor which restricts the reactivity.

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PHOTOTROPY OF TITANIUM DIOXIDE

W.E. Bull May 1, 1956

Phototropy may be defined as the reversible change of color which certain substances undergo when exposed to light of a suitable wavelength. The original color returns in the dark; the reversion is often accelerated by heating (1). This property is more commonly encountered in organic chemistry than in inorganic chemistry. Some of the general classes of organic compounds exhibiting phototropic behavior are hydrazones, osazones, anils, fulgides, triphenyl methane derivatives, and camphor derivatives. Some of the inorganic compounds which show phototropic behavior are Li_2NH, CuCl, CuBr, alkaline earth sulfides, ZnS, TiO_2 and a number of mercury compounds (2).

Tanaka (3), while studying the solid phase reaction of TiO_2 with the alkaline earth oxides, noticed that $CaTiO_3$ became red when exposed to light or x-rays. He also noted that the samples which had been prepared at 1200° were more sensitive than those prepared at 1350°, and that moisture was necessary for the color change to occur. On heating to 220°, the samples became white again. Tanaka suggested that impurities caused the photodecomposition of water, the hydrogen that was formed then reducing the titanium(IV) to titanium(III) which gave the red color.

McNevin and Ogle (4) have also studied the phototropy of the alkaline earth titanates. From the results obtained when various impurities were incorporated into the titanates, these workers concluded that the color change is due to a crystal lattice phenomenon.

The phototropic behavior of titanium dioxide was first observed by Parmelee and Badger (5) while working with titanium dioxide in ceramic glazes.

Williamson (6,7), using high purity titanium dioxide found that strong color changes could be brought about when titanium dioxide was contaminated with Fe_2O_3, 0.2% of the latter giving the most pronounced effect. He found the color change to occur only if some of the rutile form of titanium dioxide was present. He supposed that the phenomenon was caused by entrance of the impurities into the rutile lattice and there occupying certain sites.

Weyl (8), using Williamson's data and considering the structure of reduced titanium dioxide, proposed a mechanism involving the formation of iron(IV). He assumed that the iron(III) ions enter the rutile lattice, where two adjacent iron(III) ions, which are strongly polarized, may be separated by an oxygen vacancy. If sufficient energy is introduced into this grouping, electrons may become excited, leave the iron(III) ions, and take the position of the missing oxide ion. This dissociation process leads to an

ron(IV) ion which satisfies the force field of the crystal. This rocess is shown schematically in Figure 1.

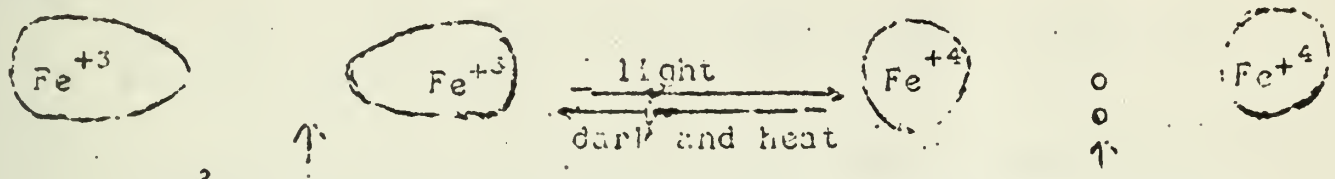

Fig. I. Schematic representation of phototropic change as proposed by Weyl.

or very low concentrations of iron, the following scheme was uggested for the transfer of electrons to an oxide ion vacancy ince the probability of two iron(III) ions being neighbors would e small.

$$Fe^{+3} + Ti^{+4} \longrightarrow Fe^{+4} + Ti^{+3}$$

$$Ti^{+3} + Fe^{+3} \longrightarrow Fe^{+2} + Ti^{+4}$$

$$Fe^{+2} \longrightarrow Fe^{+4} + 2e^{-}$$

eyl pointed out that for some materials, which contain oxide acancies, chromophoric groups may exist at room temperature ecause of the thermal vibrations in the lattice. He suggested hrome-tin pink, cadmium oxide, lead dioxide, and manganese dioxide s possible examples.

McTaggert and Bear (9) have investigated the phototropy of itanium dioxide, using various impurities and various conditions f incorporating these impurities into the samples. They found hat phototropic behavior resulted in samples, which had been eated for only a few minutes at 300° and that water was necessary or the color change to occur. These workers believe that this emperature is too low to effect the entrance of the impurity into he lattice structure. McTaggert and Bear found that only the utile form of titanium dioxide showed phototropic behavior and that he intensity of the color was inversely proportional to the rutile ontent. They also found that samples prepared in an oxygen tmosphere were not phototropic.

Considering the photochemical liberation of oxygen from itanium dioxide, which was studied by Goodeve (10,11), the ollowing mechanism was proposed.

1. The impurity ion is adsorbed on the surface of the rutile (at the interfaces in rutile-anatase mixtures) the nature of the bonding being such as to render a reduced form of the impurity the stable form.

2. On irradiation, oxygen is liberated from the titanium dioxide. This oxygen oxidizes the impurity ion to a higher valence state.

3. On cessation of irradiation, the higher valence form reverts to the lower stable form.

4. The rapid reversal of color obtained when the irradiated samples are heated may be the result of activation, in which the change of valency is accelerated.

5. The presence of water molecules plays a decisive part in the process either because of their action with the oxygen liberated from titanium dioxide or because of their entrance into the bonding between the impurity and the host oxide.

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ELECTROCHEMICAL FLUORINATION OF INORGANIC COMPOUNDS

P.N. Yocom May 15, 1956

Electrofluorination in inorganic chemistry seems to have been overlooked to a great extent even though it offers the advantage of the elimination of the handling of elemental fluorine. The subject of electrofluorination may be divided into two divisions, depending upon whether active or passive anodes are used.

The reactions at attackable anodes do not involve any particular problems and may be classified into three groups.

1. The anode material goes into solution as a positive ion. Many of the common metals show this behavior in aqueous, acidic fluoride solutions.

2. The anode material precipitates as a slightly soluble material. In anhydrous acetic acid - KF solutions AgF and K_2TaF_7 can be produced in this manner at Ag and Ta anodes.[2]

3. A strongly adhering film forms on the anode. A patent has been issued in Germany for the production of protective films on Al and Mg by this method.[3]

On the other hand, reactions at unattackable anodes, outside of the simple oxidation of cations,[4,5] present some interesting problems. It must be recognized, however, that in reality there is no such thing as a completely unattackable anode. In most of these studies nickel anodes are used; they always have a thin protective layer of nickel fluoride on them.

Latimer[6] calculates the standard potential for the reaction

$$F^- = {}^1/_2F_2 + e$$

in aqueous solution to be 2.85 volts; however, the liberation of fluorine actually requires about 8 volts. This overvoltage of 5 volts is by far the largest overvoltage ever observed and its causes are not at all clear, although concentration polarization could account for much of it.

It has been noted that in melts of KF·nHF, containing water, that OF_2 in yields up to 30% is evolved at potentials of 5 to 7 volts. The formation of this compound is attributed to the depolarizing action of water on the discharge of the fluoride ion. It is hypothesized that the mechanism involves the initial formation of the unstable hypofluorous acid, HOF, which can the decompose in either of two ways to give O_2 or OF_2.

Ruff and coworkers[8,9] have also produced in $NH_4F \cdot HF$ media the nitrogen fluorides, NH_2F, NHF_2, and NF_3, without the appearance of elemental fluorine. In these cases NH plays the role of a depolarizer for the discharge of the fluoride ion. In 1952 Engelbrecht and Atzwanger[10] reported the preparation of perchloryl fluoride, ClO_3F, by the electrolysis of $NaClO_4$ in HF. This unusual compound is now being put into commercial production. It is reported to be non-corrosive, thermally stable to the softing point of glass, not hydrolyzed by hot water and only slowly decomposed by alkali solutions.[13] However, it is a good oxidizing agent and supports combustion.

Schmidt and Schmidt have made a close study of the formation of SO_2F_2 from HSO_3F in HF in order to try to elucidate the reaction mechanism. The two reactions they postulate are as follows:

$$F - SO_2 - OH + 3HF = F - SO_2 - F + OF_2 + 2H_2 \qquad (I)$$

$$F - SO_2 - OH + HF = F - SO_2 - F + {}^1/_2O_2 + H_2 \qquad (II)$$

They followed the electrolytic reaction by separating the gases that were given off by the cell during electrolysis. Since oxygen was found in a larger relative amount than OF they conclude that reaction II predominates during electrolysis. As a result of a material balance for sulfur before and after electrolysis, they conclude that a small amount of SF is also formed.

Current voltage curves for fluoride systems have been run by Sargent and coworkers[12] and Shrivastava[11], but they do not show any conclusive results.

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THESIS REPORT

HE STRUCTURES AND STABILITIES OF SOME COMPLEX INORGANIC COMPOUNDS

. THE DETERMINATION OF WATER IN COMPLEX INORGANIC COMPOUNDS

I. THE STRUCTURES OF SOME THIOCYANATO COBALT AMMINES

lark M. Chamberlain May 22, 1956

. The Application of Karl Fischer Reagent to the Determination of Water in Inorganic Coordination Compounds

The purpose of this investigation was to determine the pplicability of Karl Fischer reagent to the differentiation of oordinated and uncoordinated water in complex inorganic compounds.

The Karl Fischer reagent (1), a mixture of pyridine, methanol, ulfur dioxide, and water, has been widely used to determine uantitatively the water content of organic and inorganic materials. nly one report has been made (2) concerning the use of this reagent n determining water in coordination compounds, and the authors tate that for unknown reasons their titrations of various aquo-ydroxy-cobalt ammines gave low, variable results.

Using a Beckman KF-1 aquameter, twenty inorganic coordination ompounds containing either coordinated water or lattice water or oth were titrated in methanol solution until an endpoint stable or thirty seconds was reached. It was hoped that this endpoint ould represent the complete titration of lattice water. After the nitial endpoint, enough additional reagent was added at one minute ntervals to return the system to a thirty second endpoint. From a lot of time vs. total volume of reagent, the second endpoint, upposedly representing complete titration of all water present, was etermined graphically.

It was found that in soluble chromium and nickel complexes, ll the water present had been titrated at the second endpoint but hat the initial endpoint was not significant. No differentiation f lattice and coordinated water could be made. Cobalt complexes, ot stabilized by chelation, gave low, variable results, probably ue to the reduction of cobalt (III) to cobalt (II) in non-toichiometric quantities (3).

I. The Structure and Stability of Some Thiocyanato Cobalt Ammines

The purpose of this investigation was to study the role of hiocyanate ion as a coordinating group. Using infrared spectro-copy and potentiometric titrations as tools it was hoped that nformation concerning the bonding between thiocyanate and the etal and that within the thiocyanato group would be obtained.

Also, two divergent views (4) (5) have been published concerning the stability of the silver addition products of the thiocyanato cobalt ammines. It was hoped to resolve these views during this study.

The chloride, thiocyanate, and perchlorate salts of $[Co(NH_3)_5NCS]^{++}$, cis and trans-$[Coen_2(NCS)Cl]^+$ and cis and trans-$[Coen_2(NCS)_2]^+$ were prepared as well as simple heavy metal thiocyanates and compounds of the type represented by $CoHg(SCN)_4$ in which thiocyanate has been shown to act as a bridge between the metals. The infrared spectra of these solid materials were obtained in mineral oil mull, and solutions of the perchlorate salts of the cobalt ammines were titrated potentiometrically with silver perchlorate.

From the results of these investigations, a resonance hybrid involving partial double bonds between cobalt and the nitrogen of the thiocyanato group has been postulated. This hybrid involves a partial triple bond between the carbon and nitrogen and a partial double bond between carbon and sulfur of the coordinated thiocyanato group, in agreement with the infrared evidence.

The potentiometric studies of the reaction between the thiocyanato cobalt ammine and silver ion indicate that no soluble stable addition product is formed in solution. The existence of solid materials containing a 1:1 ratio of complex to silver has been attributed to dipole attraction between the thiocyanato group or groups and the silver ion.

A study of the infrared spectraof the acido-bisethylenediamine cobalt (III) salts has shown that it is possible to differentiate between coordinated and ionic thiocyanate in these materials. From a comparison of the deuterated and undeuterated compounds, the frequencies peculiar to the N-H stretching deformation and wagging frequencies have been assigned.

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THESIS REPORT

STUDIES ON THE OXIDATIVE AND THERMAL STABILITY OF COMPLEX INORGANIC COMPOUNDS

W.C. Drinkard May 22, 1956

I. Relative Rates of Oxidation of Ferrous Sulfate and Ferrous Ammonium Sulfate Solutions

Over the years a great deal of work has been reported on the rate of oxidation of ferrous ion. As pointed out in an earlier seminar (1), investigators have reported conflicting evidence on the effect of various ions on the oxidation rates. Many text books of qualitative analysis suggest the use of ferrous ammonium sulfate solutions because of their slower rate of oxidation as compared to ferrous sulfate. It was the purpose of this investigation to determine the validity of this statement and, if possible, to determine the reason for the inhibition.

It has been shown that when a stream of air is bubbled through a 0.1M solution of ferrous ion, ferrous ammonium sulfate solution oxidizes more rapidly than ferrous sulfate solution. In an effort to explain the earlier conflicting reports, an investigation was made of the effect of trace amounts of Cu^{++}, K^{+}, NH_4^{+}, Mg^{++}, Zn^{++}, Mn^{++}, Ni^{++}, and Co^{++}. Copper ion resulted in a slight increase in oxidation rate while no effect could be found for the other ions.

Effect of pH during oxidation has also been investigated.

II. Coordination Polymers

Within recent years a great deal of interest has been directed toward the formation of polymers stable at high temperatures. The unusual thermal stability of many coordination compounds suggests their use for such polymer formation.

Two approaches to the formation of linear coordination polymers are:

1. Use of a difunctional ligand containing groups so arranged that coordination of both groups to the same metal is impossible.
2. Formation of coordination monomers containing two free functional groups capable of further reaction.

Compounds investigated in these classes are:

1. (a) Copper phthalocyanine derivatives as prepared from pyromellitic acid.
   (b) 8-hydroxyquinoline molecules linked through the 5 position by $-S-$, $-SO_2-$, or $-CH_2-$.
   (c) bis-(beta-diketone) Schiff bases with ethylenediamine.

In cases (b) and (c) metals of coordination number four and oxidation state of plus two would give linear polymers.

2. (a) bis-(monohydroxyethyldiethylenetriamine) cobalt(III) chloride.
   (b) bis-(N-hydroxyethylethylenediamine)copper(II) chloride.
   (c) bis-(monohydroxyethyldiethylenetriamine) nickel(II) chloride.
   (d) Trinitro-dihydroxyethyldiethylenetriamine cobalt(III).
   (e) Trithiocyanato-dihydroxyethyldiethylenetriamine cobalt(III).

The hydroxyl groups of compounds (a), (b), and (c) are inert and no reaction has been possible to date. Compounds (d) and (e) are unstable under conditions tried for polymerization.

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THESIS REPORT

ELECTROCHEMICAL STUDIES OF ETHYLENEDIAMINE AND DIMETHYLFORMAMIDE SOLUTIONS OF ANHYDROUS LANTHANUM NITRATE AND BROMIDE

G.W. Cullen May 29, 1956

This investigation is essentially the third of a series initiated by Paul Zimmerman (1) and continued by Victor Aftandilian (2). Zimmerman investigated the possibility of winning the free rare earth metals through electrodeposition from ethylenediamine solutions of rare earth acetates, halides and nitrates and ethanolamine solutions of acetates and halides. Presence of the free metals in the cathode deposits obtained from ethylenediamine solutions was indicated by the reducing character of the material. X-ray diffraction analysis did not bear out the presence of the metals.

Victor Aftandilian put a good deal of effort into the preparation of anhydrous rare earth nitrates by reaction of the rare earth oxide with N_2O_4. The possibility of employing the resulting nitrate as a solute for electro-reductions in ethylenediamine solution was studied briefly. Cathode deposits were obtained which, on vacuum heating, gave X-ray evidence for the presence of the metals.

It is the purpose of the present investigation to characterize further the processes involved in electrodeposition from ethylene-diamine with the aim of obtaining more clear cut results. Also, physical properties of dimethylformamide warrant the investigation of this material as a solvent for electro-reduction studies.

The solubilities of the anhydrous salts and the conductivities of EN and DMF solutions of anhydrous lanthanum nitrate and bromide have been determined. Comparison of solubilities obtained for the nitrate DMF system with those reported by Zimmerman and Aftandilian, and the fact that both of these investigators describe a vigorous reaction on dissolution point to the possibility that trace amounts of water were present in the EN previously employed. This is not surprising, considering the rapidity with which EN absorbs atmospheric components, and the difficulties experienced in keeping the solvent completely dry. Thus, solubilities and conductivities were measured as a function of water content of EN. The solubility of the nitrate in EN is found to change markedly even with trace amounts of water present.

Electro-reductions have been attempted in both EN and DMF solutions of lanthanum nitrate and bromide under various conditions. Preliminary experiments in the bromide-DMF system have not been encouraging even though the salt is comparatively soluble in this medium. The bromide is so insoluble in dry EN that this system offers little promise. Electro-reductions in the nitrate-EN system containing trace amounts of water have offered the greatest encouragement. X-ray diffraction patterns of the dark cathode deposit

obtained in this system contain some lines which may be assigned to metallic lanthanum. The qualitative analysis is, however, tremendously confused by the coincidence of both lanthanum hydroxide and oxide diffraction lines with those of the free metal. On microscopic examination the dried deposit appears to be a light homogenous and non-crystalline material. After vacuum heating, the deposit is dark, granular, and non-homogeneous. Reactions carried out on the microscope stage with various reagents indicate that the heated material may consist of occlusions of the dark metal in a matrix of the oxide.

This investigation has not as yet been entirely completed.

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THESIS REPORT

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

Chui Fan Liu May 29, 1950

I. Isomerism of the Dinitro-ethylenediamine-2,3-butylenediamine-cobalt(III) Ion.

In 1918 Werner reported the separation of all the eight possible isomers of Cis-Co en pn$(NO_2)_2^+$. The isomerism of this compound involves three different factors:

A. The asymmetry of the cobalt.
B. The asymmetry of the diamine.
C. The unsymmetrical location of the methyl group on the propylenediamine.

The problem may be simplified by taking only two factors into consideration at a time. This was done by using other diamines than propylenediamine. Corbax prepared the compound Cis-Co en ibn$(NO_2)_2^+$ and separated the four possible isomers. In this compound only factors A and C are operative.

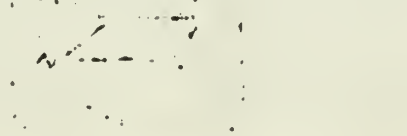
The present problem involves the same type of compound except that 2,3-butylenediamine is used in place of iso-butylenediamine. In this case two methyl groups are unsymmetrically located and only factors A and B need be considered. The compound should have four isomers. By investigation of the d-, l-, meso-dimethyl-m-sulfonate all four isomers were obtained. These are not all of equal stability, and some of them have not been obtained in optically pure form.

II. Cobalt (III) Complexes of Nitrilotriethylamine and Its Schiff's Base with Salicylaldehyde.

Nitrilotriethylamine forms cobalt(III) complexes which possess high stabilities and the desirable property of being Cis and symmetrical molecules. Such complexes may be used in a large number of stereochemical problems.

The Cobalt(III) complexes are very difficult to obtain by oxidation of Cobalt (II) in the presence of the amine. However, if a cobalt(III) complex is used as starting material complexes with nitrilotriethylamine may be obtained with ease. $[Co\ trian(OH_2)_2]Cl_3$ and $[Co\ trian\ Cl_2]Cl$ were obtained by this method. These complexes will be used to study the stereochemistry of mono-tertrade complexes.

When nitrilotriethylamine was treated with salicylaldehyde the Schiff's base containing three molecules of salicylaldehyde per molecule of amine was obtained. This Schiff's base formed a water insoluble cobalt(III) complex. From preliminary studies this complex appeared to have the structure



If this is the case the resolution of this complex into its d and l isomers will be extremely interesting.

THESIS REPORT

THE RESOLUTION OF ORGANIC COMPOUNDS VIA COORDINATION

Bennie A. Ferrone May 29, 1956

Classically, three methods exist for the resolution of racemic mixtures: (1) mechanical resolution, (2) bacterial resolution, and (3) chemical resolution. More recently developed methods of resolution involve adsorption and paper chromatography. Of all the methods available, chemical resolution is used most often.

A different approach to chemical resolution involves the use of optically active coordination compounds. In this case, resolution occurs because of preferential coordiation of one of the optical antipodes. The general scheme is:

D-(or L-) $[Co(l\text{- or } d\text{-}AA)_2Cl_2]Cl$ + 2d1-BB →

D-(or L-)$[Co(l\text{- or } d\text{-}AA)_2(l\text{- or } d\text{-}BB)]Cl_3$ + d-or l-BB

(where AA and BB = bidentate groups).

The work reported here has been concerned with complexes of stilbenediamine (= stien). The complex, trans-$[Co(l\text{-stien})_2Cl_2]Cl$, has been prepared. It was hoped that the following reactions would go as shown:

1. trans-$[Co(l\text{-stien})_2Cl_2]Cl$ + 2d1-stien → $[Co(l\text{-stien})_3]Cl_3$ + d-stien

2. trans-$[Co(l\text{-stien})_2Cl_2]Cl$ + 6d1-pn → $[Co(l\text{-pn})_3]Cl_3$ + 2 l-stien + 3 d-pn

3. 2 trans-$[Co(l\text{-stien})_2Cl_2]Cl$ + 6 Ag_2 di-tart →

$[Co(l\text{-stien})_2(d\text{-tart})]_2$ d-tart + 6AgCl + 3 Ag_2 l-tart

In cases 2 and 3, no resolutions were observed. The results in case 1 are not conclusive as yet.

Another reaction has been tried in which d-phenylalanine replaced all the stilbenediamine molecules in $[Co(\underline{rac}\text{-stien})_3]Cl_3$. In this case, only one-half the theoretical amount of d-phenylalanine was used, and it was hoped that a preferential replacement would occur. However, polarimetric results showed that such was not the case.

Other reactions are being tried in attempts to show resolution by preferential coordination. In addition, wherever possible, the factors affecting resolution are being studied. A kinetic study will be carried out on the reaction of the <u>dextro</u>, <u>levo</u>, and <u>meso</u> forms of stilbenediamine with trans-$[Co(l\text{-stien})_2Cl_2]Cl$.

THESIS REPORT

COORDINATION COMPOUNDS OF P,P,P',P'-TETRAETHYLETHYLENEDIPHOSPHINE

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Complex compounds of ethylenediamine and other nitrogen bases capable of forming five-membered chelate rings are well known. The purpose of this investigation was to prepare similar phosphorus compounds of the type $R_2PCH_2CH_2PR_2$ and to study their coordination compounds.

Tetraethylethylenediphosphine (TEP) was prepared according to the following reactions, using liquid ammonia as a solvent at -70°C.

$$2Na + 2PH_3 \rightarrow NaPH_2 + H_2 \quad (1)$$
$$NaPH_2 + C_2H_5Br \rightarrow C_2H_5PH_2 + NaBr \quad (2)$$
$$C_2H_5PH_2 + NaNH_2 \rightarrow C_2H_5PHNa + NH_3 \quad (3)$$
$$C_2H_5PHNa + C_2H_5Br \rightarrow (C_2H_5)_2PH + NaBr \quad (4)$$
$$(C_2H_5)_2PH + NaNH_2 \rightarrow (C_2H_5)_2PNa + NH_3 \quad (5)$$
$$2(C_2H_5)_2PNa + ClCH_2CH_2Cl \rightarrow (C_2H_5)_2PCH_2CH_2P(C_2H_5)_2 + 2NaCl \quad (6)$$

The sodium salts shown in equations (3) and (5) may contain solvated ammonia or a chemically bonded amide ion (1).

Air oxidation in alcohol was used to prepare diamagnetic cobalt(III)complexes of the formula $[Co(TEP)_2X_2]X$ (X= Cl, Br or I). These compounds are ionic as indicated by their conductance in nitrobenzene and the molar conductance of the chloro compound (120 ohms^{-1}) at a dilution of 1024 liters. Thus they are the usual hexacovalent cobalt(III) complexes with d^2sp^3 bonding. By working in a nitrogen atmosphere, two cobalt(II) complexes of the formulas $[Co(TEP)Br_2]$ and $[Co(TEP)_2]I_2$ were prepared. The green bromo complex has three unpaired electrons and is non-conducting in nitrobenzene, which indicates a tetrahedral configuration. The brown iodide compound has one unpaired electron and is conducting in nitrobenzene, which suggests planar dsp^2 bonding. These cobalt(II) compounds are unusual because the number of coordinated ligands appears to determine the configuration of the cobalt. Thus the bromo complex containing one diphosphine is tetrahedral, while the iodine compound containing two coordinated diphosphines is probably planar. It is doubtful if the different halogens could be responsible for this change.

The complexes $[Ni(TEP)X_2]$ (X= Cl or Br) and $[Ni(TEP)_2](ClO_4)_2$ were prepared. They are diamagnetic and therefore supposedly planar. Oxidation of $Ni(TEP)Br_2$ with bromine gave a green-black compound of the composition $Ni(TEP)Br_3$. It has one unpaired electron, confirming the presence of nickel(IV).

With the coinage metals, the compounds $[Cu(TEP)_2]$ $[Cu(TEP)I_2]$, $[Ag(TEP)_2]AgI_2$ and $IAuEt_2PCH_2CH_2PEt_2AuI$ have been prepared. The first two are conducting in nitrobenzene, but the gold(I) complex is non-conducting. Its molecular weight was confirmed ebullioscopically in chloroform. This white gold(I) complex was oxidized by iodine to a black gold(III) compound, the analysis of which corresponds to the formula $I_3AuEt_2PCH_2CH_2PEt_2AuI_3$.

Other compounds prepared were $[M(TEP)Br_2]$ (M = Zn, Cd or Hg), $[Pb(TEP)Br_2]$, $[Pb(TEP)_2](ClO_4)_2$ and $[Pd(TEP)Cl_2]$. Attempts to coordinate two diphosphines to palladium failed.

REFERENCES

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